A Thesis

CRYSTAL STRUCTURE ANALYSES OF CLATHRATES AND ORGANIC COMPOUNDS

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by

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Summary

The thesis is divided into three parts: the first part is a brief review of the theory and methods of X-ray crystallography and the second and third parts contain accounts of seven crystal structure analyses in the fields of clathrate and organic chemistry respectively.

Clathrates may be defined as molecular compounds having a regular cage structure of one component (the host compound), which physically encloses the other component or components (the guest compound). The great scientific interest of clathrate compounds and the widespread occurrence of these and related inclusion compounds in nature has aroused interest in the structure of these compounds. In order to determine the structure of the host molecular framework of the cage of the clathrates formed by 4-p-hydroxyphenyl-2,2,4-trimethylchroman (Dianin's compound) and 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman and in order to obtain information concerning the effect of host-guest molecular interactions on the orientation and conformation of guest molecules within the cavity of the clathrates formed by 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman, the analyses presented in Part II were undertaken.

The analyses establish that the host molecules of the chroman and thiachroman clathrates are linked together by a network of

hydrogen bonds and van der Waals' forces to form distinct cages, the cavities of which have an approximate hourglass shape. In addition it has been possible, by X-ray methods, to define the orientation, conformation and dimensions of a guest molecule, 2,5,5-trimethylhex-3-yn-2-ol, within the cavity of the clathrate formed by 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman. It is found that the staggered conformation adopted by this conformationally labile guest molecule within the cavity is imposed upon it by the van der Waals' surface of the cavity.

Part III contains the crystal structure analyses of four compounds, viz., 2,7-dihydro-3,6-di-p-tolyl-1,4,5-thiadiazepine-1,1-dioxide; 2,4-dimethyl-1,5-benzodiazepinium bromide; 3,7-dibromo-cycloocta-1,5-diene and dioscorine methobromide which were undertaken in order to obtain quantitative information concerning the stereochemistry and conformation of these compounds.

The structure analyses of 2,7-dihydro-3,6-di-p-tolyl-1,4,5-thiadiazepine-1,1-dioxide and 2,4-dimethyl-1,5-benzodiazepinium bromide have succeeded in showing that the seven-membered unsaturated heterocyclic rings adopt a boat and planar conformation respectively.

It has been known for more than twenty years that allylic bromination of cycloocta-1,5-diene yields a di-bromide derivative. Earlier chemical and spectroscopic studies of this derivative did

not lead to a successful structure determination. The molecular structure of the di-bromide has now been definitely established as 3,7-dibromocycloocta-1,5-diene by X-ray analysis. This has shown that 3,7-dibromocycloocta-1,5-diene adopts a twist-tub conformation in the solid state.

Although the structure of dioscorine, an alkaloid isolated from the tubers of Dioscorea hirsuta, Blume and Dioscorea hispida, Dennst., found in Java and the Philippine islands respectively, has been established by synthesis, the stereochemistry of the attachment of the lactone group was not unambiguously established. The X-ray analysis has succeeded in showing that the structure consists of an iso-quinuclidine residue to which an unsaturated δ - lactone is spiro linked. The results suggest that the unsaturated δ - lactone ring adopts a flattened half-boat conformation, in general agreement with the results obtained for other saturated δ - lactones.

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Crystal Structure Analyses of Organic Compounds

PART I

SOME METHODS OF X-RAY ANALYSIS

1.1 Introduction

By 1894, a date prior to the discovery of X-rays by Rontgen, the geometrical theory of crystal structure had been completely elucidated independently by Fedorow, Schoenflies and Barlow. However the a priori deduction of three-dimensional models of possible structures on this basis proved to be a much more difficult problem.

The solution to this problem lay in von Laue's realisation that if X-radiation had a wavelength comparable in magnitude to the distance between adjacent atoms in solids, then a crystal would provide a suitable three-dimensional diffraction grating for X-rays. The experimental test of von Laue's hypothesis was undertaken by Friedrich and Knipping. After a number of unsuccessful trials, a diffraction of the primary beam was observed. Thus a powerful new tool became available for investigating the structure of matter on an atomic scale.

This consequence, however, did not follow immediately, nor were the first results easy to interpret. In particular, ZnS which was used in the early investigations was assigned a primitive cubic structure. However, since the ZnS crystal gave only a selection of the diffracted beams that von Laue expected, he explained this by ascribing to the atoms a strongly selective scattering power for X-rays and was thus led to believe in the existence of five characteristic wavelengths in the radiation.

A great advance and simplification was effected when the work was taken up in England by W.H. and W.L. Bragg. The success of W.L. Bragg's treatment of the problem was based on his introduction of the idea of reflection of X-rays from crystal planes and his realisation that in the Laue experiment the X-ray beam was heterogeneous, consisting of a continuous range of wavelengths. By means of this interpretation, W.L. Bragg was able to show that the Laue photographs of NaCl and KCl could be explained by one of the structures postulated for these compounds before the Laue experiments by Pope and Barlow. Within a short time the structures of many simple inorganic substances were determined.

In the field of organic chemistry, however, the progress was at first slow, due both to the greater difficulty of determining the electron density distribution from the X-ray intensities and to the scale of the calculations involved. The discovery of the so called "heavy atom" and "direct methods" of extracting phase information from the intensities obtained with heavy atom and equal atom structures respectively and the advent of the electronic computer have removed these problems to a large extent.

In its present state of development, X-ray crystallography is now the most powerful method available for the detailed study of structure and bonding in molecules.

1.2 The Geometry of X-ray Diffraction

Consider a beam of monochromatic X-rays of wavelength λ to be incident upon a crystal in a direction defined by the unit vector $\lambda\underline{s}_o$ (Fig. 1.1). The path difference between the wave scattered at a point A in a direction defined by the unit vector $\lambda\underline{s}$ is, relative to the wave scattered at the origin O in the same direction,

$$OB - AC = \lambda\underline{r}.\underline{s} - \lambda\underline{r}.\underline{s}_o = \lambda\underline{r}.(\underline{s} - \underline{s}_o) = \lambda\underline{r}.\underline{S} \qquad (1)$$

where $\underline{r}$ is the vector position of A relative to the origin and $\underline{S} = \underline{s} - \underline{s}_o$. The vector $\underline{S}$ defines the spatial relationship of the incident and diffracted beams. From Fig. 1.2 it can be seen that, if the angle between the incident and diffracted beams is 2θ, then

$$\underline{S} = 2 \sin \theta/\lambda \qquad (2)$$

The path difference $\lambda\underline{r}.\underline{S}$ corresponds to a phase difference of $2\pi\underline{r}.\underline{S}$. If the electron density at A in electrons per unit volume is $\rho(\underline{r})$, then the wave scattered by the electron density in the volume element dV about A, relative to the wave scattered by a single electron at the origin is defined, both in amplitude and phase, by

$$G_A(\underline{S}) = \rho(\underline{r})dV.\exp 2\pi i\underline{r}.\underline{S} \qquad (3)$$

In a crystal with lattice translations $\underline{a}$, $\underline{b}$ and $\underline{c}$, the

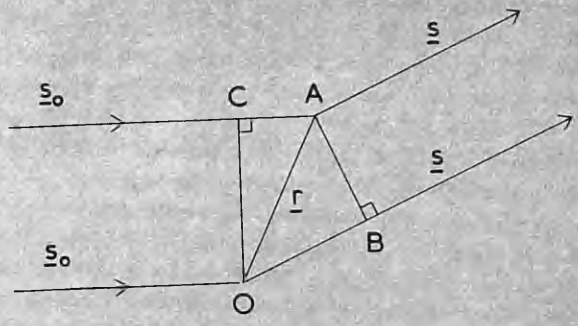


Fig. 1.1

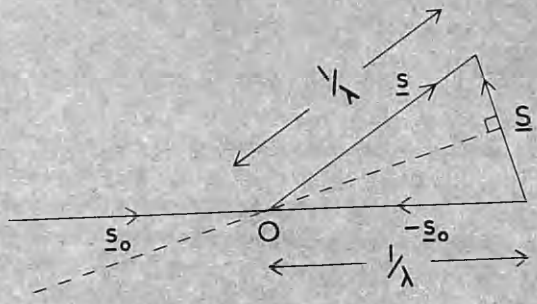


Fig. 1.2

electron densities at the points which lie on the lattice defined by the vector equation

$$\underline{R} = \underline{r} + u\underline{a} + v\underline{b} + w\underline{c} \tag{4}$$

where u, v and w are any three integers, will be identical since the electron density $\rho(\underline{r})$ is periodic. The wave scattered in the direction $\lambda\underline{s}$ from any one of these points, say B, is therefore

$$\begin{aligned} G_B(\underline{S}) &= \rho(\underline{r})dV.\exp 2\pi i\underline{R}.\underline{S} \\ &= G_A(\underline{S}).\exp 2\pi i(u\underline{a} + v\underline{b} + w\underline{c}).\underline{S} \end{aligned} \tag{5}$$

The path difference between the waves is therefore $\lambda(u\underline{a} + v\underline{b} + w\underline{c}).\underline{S}$. For the wave scattered by the crystal to have maximum intensity, the path difference between $G_A(\underline{S})$ and $G_B(\underline{S})$ must be an integral number of wavelengths. This condition is given by

$$\lambda(u\underline{a} + v\underline{b} + w\underline{c}).\underline{S} = n\lambda \tag{6}$$

where n is an integer, for all values of u, v and w. Hence

$$\begin{aligned} \underline{a}.\underline{S} &= h \\ \underline{b}.\underline{S} &= k \\ \underline{c}.\underline{S} &= l \end{aligned} \tag{7}$$

where h, k and l are integers. The equations (7) are known as the Laue equations.

$\underline{a}.\underline{S} = h$ defines a family of planes normal to $\underline{a}$. The separation between any two adjacent planes is $1/|\underline{a}|$.

Similarly $\underline{b}.\underline{S} = k$ and $\underline{c}.\underline{S} = l$ represent families of planes normal to $\underline{b}$ and $\underline{c}$ respectively. Since $\underline{a}$, $\underline{b}$ and $\underline{c}$ are never parallel, the Laue equations (7), define three sets of planes whose intersections form a lattice in the space of $\underline{S}$. If the primitive translations of the lattice are $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$, then the lattice is defined by the equation

$$\underline{S} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^* \tag{8}$$

From equations (7) and (8), it follows that $\underline{a}^*$ is normal to $\underline{b}$ and $\underline{c}$ and that the projection of $\underline{a}^*$ upon $\underline{a}$ is $1/|\underline{a}|$. Similar results follow for $\underline{b}^*$ and $\underline{c}^*$. The primitive translations of the lattice defined by (8), which is termed the reciprocal lattice of the crystal, are related to the primitive translations of the real space lattice of the crystal by

$$\begin{aligned} \underline{a}^* &= \underline{b}\times\underline{c}/V \\ \underline{b}^* &= \underline{c}\times\underline{a}/V \\ \underline{c}^* &= \underline{a}\times\underline{b}/V \end{aligned} \tag{9}$$

where V is the volume of the unit cell in real space.

The Laue equations (7) may be rewritten in the form

$$(\underline{a}/h).\underline{S} = (\underline{b}/k).\underline{S} = (\underline{c}/l).\underline{S} = 1 \tag{10}$$

By definition, $\underline{a}/h$, $\underline{b}/k$ and $\underline{c}/l$ are the intercepts on the crystal axes of the plane with Miller indices (hkl).

From (10), the projections of three points in this plane on to $\underline{S}$ are equal. $\underline{S}$ is therefore normal to the plane and $|\underline{S}| = 1/d_{hkl}$, where d_{hkl} is the origin to plane distance. Substituting in equation (2) for $|\underline{S}|$ yields

$$2d_{hkl} \sin\theta = \lambda \qquad (11)$$

From Fig. 1.2 it can be seen that $\underline{s}$ and $\underline{s}_o$ make equal angles θ with the plane which is normal to $\underline{S}$. Thus diffraction by a crystal may be regarded as reflection from the crystal plane with Miller indices (hkl). This treatment is due to W.L. Bragg (1913).

1.3 The Structure Factor

The wave, $G(\underline{S})$, scattered by the entire contents of one unit cell is completely defined by

$$G(\underline{S}) = \int \rho(\underline{r}) \exp 2\pi i \underline{r}.\underline{S} \, dV \tag{12}$$

where the integration is taken over the volume of one unit cell. $G(\underline{S})$ is thus the Fourier transform of the electron density distribution.

If the unit cell contains N atoms, the electron density function $\rho(\underline{r})$, may be regarded as the sum of N independent atomic electron densities and the total wave scattered by the unit cell may be regarded as the sum of the waves scattered by the N individual atoms and is therefore

$$G(\underline{S}) = \sum_{n=1}^{N} \int_{-\infty}^{+\infty} \rho_n(\underline{r}) \exp\left\{2\pi i(\underline{r} + \underline{r}_n).\underline{S}\right\} dV \tag{13}$$

where $\rho_n(\underline{r})$ is the electron density distribution of the n^{th} atom referred to an origin in the atom. The vector position of the n^{th} atom with respect to the origin of the unit cell is defined by

$$\underline{r}_n = \underline{x}_n + \underline{y}_n + \underline{z}_n \tag{14}$$

where $\underline{x}_n$, $\underline{y}_n$ and $\underline{z}_n$ are the atomic coordinates.

The function

$$f_n(\underline{S}) = \int_{-\infty}^{+\infty} \rho_n(\underline{r}) \exp 2\pi i \underline{r}.\underline{S} \, dV \tag{15}$$

is the Fourier transform of the atomic electron density and is termed the atomic scattering factor. If the atom is assumed to be centrosymmetric, the function $f_n(\underline{S})$ is real, if the origin of $\underline{r}$ has been taken at the centre of symmetry; if $\rho_n(\underline{r})$ is spherically symmetric and hence a function of $|\underline{r}|$ only, $f_n(\underline{S})$ is a function of $|\underline{S}| = 2 \sin\theta/\lambda$ only (from (2)).

The function $f_n(\underline{S})$ defines the wave scattered from a point $\underline{r}$ in the atom, relative to that scattered by a single electron. Phase differences arise between the waves scattered at different parts of the same atom and are a function only of the scattering angle. Such phase differences increase with scattering angle and accordingly the amplitude of the total wave scattered by the atom, and hence $f_n(\underline{S})$, decreases as $\sin\theta/\lambda$ increases.

Since $\rho_n(\underline{r})$ is known accurately only for the isolated hydrogen atom, the scattering factors for other atoms are, in general, only approximate. Tabulated values of the atomic scattering factors, calculated on the basis of spherical atomic symmetry are given in International Tables for X-ray Crystallography, Volume III, (1962).

Substitution of (15) into (13) gives

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp 2\pi i \underline{r}_n \cdot \underline{S} \qquad (16)$$

The total wave scattered by the crystal has an appreciable

amplitude only if the Laue equations (7) are simultaneously satisfied; that is, when

$$\underline{S} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^* \tag{8}$$

If the fractional coordinates of the n^{th} atom with respect to the crystal axes are x_n, y_n and z_n then equation (14) may be rewritten as

$$\underline{r}_n = x_n\underline{a} + y_n\underline{b} + z_n\underline{c} \tag{17}$$

Substitution of (17) and (8) into (16) gives

$$\begin{aligned} G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S})\exp 2\pi i(&hx_n\underline{a}.\underline{a}^* + kx_n\underline{a}.\underline{b}^* + lx_n\underline{a}.\underline{c}^* \\ &+ hy_n\underline{b}.\underline{a}^* + ky_n\underline{b}.\underline{b}^* + ly_n\underline{b}.\underline{c}^* \\ &+ hz_n\underline{c}.\underline{a}^* + kz_n\underline{c}.\underline{b}^* + lz_n\underline{c}.\underline{c}^*) \end{aligned} \tag{18}$$

From the definition of the reciprocal lattice, it can be shown that $\underline{a}.\underline{a}^* = 1$ and $\underline{a}.\underline{b}^* = \underline{a}.\underline{c}^* = 0$ and similarly for $\underline{b}$ and $\underline{c}$. Hence it is found that

$$\underline{r}_n.\underline{S} = hx_n + ky_n + lz_n \tag{19}$$

Substitution of (19) into (16) gives the structure factor expression

$$G(\underline{S}) = F(hkl) = \sum_{n=1}^{N} f_n(hkl)\exp 2\pi i(hx_n + ky_n + lz_n) \tag{20}$$

The structure factor, F(hkl), is a special value of the Fourier transform of the electron density distribution which can

only be observed when the Laue equations (7) are satisfied, that is, when the vector $\underline{S}$ takes values which result in the total wave scattered by one unit cell of the crystal having a non-zero amplitude. The structure factor then describes the amplitude and phase of the wave scattered by one unit cell and, since all unit cells must scatter in phase, also describes the amplitude and phase of the total wave scattered by the crystal. F(hkl) is, in general, a complex quantity and may be written

$$F(hkl) = G(\underline{S}) = A + iB \tag{21}$$

where

$$A = \sum_{n=1}^{N} f_n(hkl)\cos 2\pi(hx_n + ky_n + lz_n) \tag{22}$$

and

$$B = \sum_{n=1}^{N} f_n(hkl)\sin 2\pi(hx_n + ky_n + lz_n) \tag{23}$$

The modulus of the structure factor, $|F(hkl)|$, termed the structure amplitude, and the phase angle, $\alpha(hkl)$, are defined by

$$|F(hkl)| = (A^2 + B^2)^{1/2} \tag{24}$$

and

$$\alpha(hkl) = \tan^{-1} B/A \tag{25}$$

If the origin of the unit cell is taken at a centre of symmetry, then B = 0 and $\alpha(hkl)$ is restricted to the values 0° or 180°.

The atomic scattering factor is normally calculated from the electron density of an isolated atom at rest. In the crystal, however, atoms have an appreciable thermal motion at room temperature. The effect of this thermal motion is to cause atoms which would scatter in phase to scatter slightly out of phase, thus reducing the amplitude of the scattered wave. This makes the electron density of the atom in the crystal appear to be more diffuse than that of the isolated atom. To allow for this effect it is necessary to replace the atomic scattering factor in the structure factor expression by the transform of the electron density of the vibrating atom. If the smearing function, $t(\underline{x})$, gives the probability that the atomic centre is at $\underline{x}$, the origin of $\underline{x}$ being taken at the maximum of the electron density of the vibrating atom, then the electron density of the vibrating atom $\rho_v(\underline{r})$ is given by

$$\rho_v(\underline{r}) = \int_{-\infty}^{+\infty} \rho(\underline{u}) t(\underline{r}-\underline{u})\, d\underline{u} \qquad (26)$$

where $\rho(\underline{u})$ is the electron density of the atom at rest. $\rho_v(\underline{r})$ is thus the convolution of $\rho(\underline{u})$ and $t(\underline{x})$, and its transform is the product of the transform of $t(\underline{x})$ and the atomic scattering factor.

Waller (1927) and Bloch (1932), showed that for an atom vibrating in an isotropic harmonic potential, the smearing function, $t(\underline{x})$, is Gaussian and that its transform is given by

$$q(\underline{S}) = \exp -2\pi^2 U \underline{S}^2 = \exp -8\pi^2 U \sin^2\theta/\lambda^2 \qquad (27)$$

where $U = \overline{u^2}$ and $(\overline{u^2})^{1/2}$ is the root mean square amplitude of vibration.

In general, however, atoms vibrate with different amplitudes in different directions and the electron density is smeared over a small anisotropic volume which may be regarded as a triaxial ellipsoid. Each non-equivalent atom may then be described by a different ellipsoid and, in general, the ellipsoids will be differently orientated. The vibration of the atom may then be described by a symmetrical third order tensor $\underline{U}$ and the mean square amplitude of vibration in the direction of the unit vector $\underline{l} = \underline{l}_1 + \underline{l}_2 + \underline{l}_3$ is

$$\overline{\underline{u}^2} = \sum_{i=1}^{i=3} \sum_{j=1}^{j=3} \underline{U}_{ij} \cdot \underline{l}_i \cdot \underline{l}_j \qquad (28)$$

where $\underline{U}$ and $\underline{l}$ are referred to the reciprocal lattice axes $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$. The transform of the smearing function becomes, for an atom vibrating with anisotropic motion,

$$q(\underline{S}) = \exp -2\pi^2 (U_{11}h^2\underline{a}^{*2} + U_{22}k^2\underline{b}^{*2} + U_{33}l^2\underline{c}^{*2} + 2U_{23}kl\underline{b}^*.\underline{c}^* + 2U_{31}lh\underline{c}^*.\underline{a}^* + 2U_{12}hk\underline{a}^*.\underline{b}^*) \qquad (29)$$

(Cruickshank, 1965).

1.4 The Fourier Series Representation of the Electron Density

The electron density function, $\rho(\underline{r})$, is a finite, single valued function which is periodic in three dimensions. It may therefore be represented by a three dimensional Fourier series. If u, v and w are integers and x, y and z are fractional coordinates, then

$$\rho(\underline{r}) = \rho(xyz) = \sum_{u}\sum_{-\infty}^{+\infty}\sum_{v}\sum_{w} A(uvw)\exp -2\pi i(ux + vy + wz) \qquad (30)$$

The structure factor F(hkl) is the Fourier transform of the electron density $\rho(xyz)$. Therefore

$$F(hkl) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\exp 2\pi i(hx + ky + lz)dx.dy.dz \qquad (31)$$

Substituting the Fourier series (30) for $\rho(xyz)$ in (31) and rearranging gives

$$F(hkl) = V\sum_{u}\sum_{-\infty}^{+\infty}\sum_{v}\sum_{w}\int_0^1\int_0^1\int_0^1 A(uvw)\exp 2\pi i(h - u)x.\exp 2\pi i(k - v)y \times \exp 2\pi i(l - w)z\, dx.dy.dz \qquad (32)$$

The triple integral in (32) is zero unless h = u, k = v and l = w. Thus

$$F(hkl) = V.A(uvw) \qquad (33)$$

which on substitution in (30) gives

$$\rho(xyz) = \frac{1}{V}\sum_{h}\sum_{-\infty}^{+\infty}\sum_{k}\sum_{l} F(hkl)\exp -2\pi i(hx + ky + lz) \qquad (34)$$

Thus the electron density function may be represented by a three dimensional Fourier series in which the coefficients are the structure factors scaled by the reciprocal of the unit cell volume.

1.5 The Measurement of Structure Amplitudes

The total energy E(hkl) which is reflected from the crystal plane with Miller indices (hkl) when a small crystal rotates with uniform angular velocity about an axis normal to the incident X-ray beam is given by

$$E(hkl) = K.L(hkl).p(hkl).|F(hkl)|^2 \qquad (35)$$

where K is a constant for the experiment and is given by

$$K = \frac{I_o \lambda^3 N^2 dV}{\omega} \cdot \frac{e^4}{m^2 c^4} \qquad (36)$$

where:-

I_o is the intensity of the incident beam,

λ is the wavelength of the X-radiation,

N is the number of unit cells per unit volume,

dV is the volume of the crystal irradiated,

ω is the angular velocity of the crystal,

e is the electronic charge,

m is the mass of the electron, and

c is the velocity of light.

The Lorentz factor, L(hkl), allows for the varying angular velocities with which the reciprocal lattice points pass through the surface of the sphere of reflection and is therefore dependent on the experimental conditions used. Since the angular velocity of

the planes is dependent on the angle between the incident beam and the plane normal to the rotation axis of the crystal, a rotation factor is normally incorporated in the Lorentz factor. The correction to be applied in the case of equi-inclination Weissenberg geometry is given by Tunell (1939) as

$$L(hkl) = \sin\theta.(\cos^2\mu - \cos^2\theta)^{-1/2}.(\sin 2\theta)^{-1} \qquad (37)$$

where μ is the angle between the incident beam and the plane normal to the rotation axis of the crystal.

If the X-ray beam incident on the crystal is unpolarised, the electric vector of the beam will be randomly orientated. However since the component of the electric vector normal to the reflecting plane will be reduced by an amount which is proportional to the reflecting angle θ, the partial polarisation of the diffracted beam produced results in a reduction of its intensity. The correction for this effect, which is independent of the experimental conditions, is given by

$$p(hkl) = (1 + \cos^2 2\theta)/2 \qquad (38)$$

The energy of the diffracted beam is proportional to its intensity, I(hkl). Thus from (35)

$$I(hkl) \propto L(hkl).p(hkl).|F(hkl)|^2 \qquad (39)$$

The intensity of the diffracted beam may be measured either

from the blackening produced on a photographic film or by the number of quanta detected in the diffracted beam by a radiation counter. From (39) the structure amplitude $|F(hkl)|$ of a Bragg reflection with Miller indices (hkl) may be measured experimentally, on a relative scale. Several methods have been proposed for placing the structure amplitudes on an absolute scale. The absolute scale may be determined by experimental comparison with a standard reflection from a standard crystal (Robertson, 1934). Alternatively, it may be deduced from the decrease in average structure amplitude with scattering angle (Wilson, 1942) or, at a somewhat later stage in the analysis, by comparison with the structure factors calculated from a reliable model of the structure.

Although equations (35) and (39) are strictly applicable only to ideal microscopic crystals, they are also applicable to the ideally imperfect macroscopic crystals used in diffraction experiments. Such crystals have a mosaic structure in which their lattice contains regions of disregistry, and they behave like an aggregation of approximately alligned microscopic crystals rather than a single block of ideal crystal (Darwin, 1914). However, the intensity of the beam diffracted from a mosaic crystal is affected by physical factors, the most important of which are absorption, primary extinction and secondary extinction, and, if neglected, they may lead to

systematic errors in the structure amplitudes calculated by equation (39).

Since X-radiation is absorbed by matter, there will be a reduction in the intensity of the emergent beam in comparison with that of the incident beam when X-rays travel through a crystal. The relationship between the intensities of the incident and emergent beam is given by

$$I = I_o \, e^{-\mu t} \tag{40}$$

where I_o is the intensity of the incident beam, μ is the linear absorption coefficient of the material and t is the distance the beam travels through the crystal. Since the path length through a crystal bounded by morphologically non-equivalent faces will, in general, be different for each plane which satisfies the Bragg reflecting conditions, rigorous correction for absorption is difficult although approximate correction for the effect is possible for crystals of spherical or cylindrical shape.

It is a consequence of the geometry of X-ray diffraction that the beam reflected from a set of crystal planes obeys the Bragg reflection condition for these planes and may therefore be reflected again. Such a doubly reflected beam is parallel to the incident beam and exactly out of phase with it. This effect is known as primary extinction and results in the beam incident on the lower

layers of the crystal being weaker than the beam incident on the upper layers. The effect is not, in general, a source of major error in the structure amplitudes obtained for diffraction from a mosaic crystal.

Secondary extinction arises from the attenuation of the incident beam, as it penetrates the crystal, by planes which satisfy the Bragg reflection condition. The intensity of the beam incident on a crystal plane is therefore the intensity of the incident beam less that which has been reflected by any plane preceding the plane under consideration. The effect is most pronounced for reflections in which the general level of intensity is high.

1.6 The Phase Problem

The calculation of the electron density distribution in a crystal by means of a Fourier series requires a knowledge of both the amplitudes and phases of the structure factors F(hkl). Although the structure amplitudes may be obtained experimentally by observing the relative intensities of the diffracted beams, there is no known experimental method whereby the relative phase angles may be determined. This constitutes the phase problem of X-ray crystallography.

A number of methods of surmounting this problem have been devised. Of these the most widely applicable have been the heavy atom method together with the related method of isomorphous substitution, and the so called direct methods.

1.6.1 The Patterson Function

The function defined by Patterson (1934; 1935) may be considered as the self-convolution of the electron density. It is defined by the expression

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz).\rho(x+u, y+v, z+w)dx.dy.dz \qquad (41)$$

where u, v and w are fractional coordinates. If the electron density expressions derived from equation (34) are substituted in (41) then

$$P(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_l\sum_{h'}\sum_{k'}\sum_{l'} F(hkl)\exp -2\pi i(hx+ky+lz)\ x$$

$$F(h'k'l')\exp -2\pi i(h'x+k'y+l'z)\exp -2\pi i(h'u+k'v+l'w)$$

$$dx.dy.dz$$

$$= \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_l\sum_{h'}\sum_{k'}\sum_{l'} F(hkl)F(h'k'l')\exp -2\pi i(h+h')x.$$

$$\exp -2\pi i(k+k')y\ x\ \exp -2\pi i(l+l').\exp -2\pi i(h'u+k'v+l'w)$$

$$dx.dy.dz \qquad (42)$$

The triple integral in (42) is zero unless $h = -h'$, $k = -k'$ and $l = -l'$. Thus

$$P(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l F(hkl).F(\bar{h}\bar{k}\bar{l})\exp\ 2\pi i(hu + kv + lw) \qquad (43)$$

Since $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ are complex conjugates

$$F(hkl).F(\bar{h}\bar{k}\bar{l}) = |F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2 \qquad (44)$$

and the Patterson function may therefore be written

$$P(uvw) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)|^2\exp\ 2\pi i(hu + kv + lw) \qquad (45)$$

Since the coefficients of the Fourier series are the squares of the structure amplitudes the Patterson function may always be

computed as only a knowledge of the structure amplitudes is required and these quantities may be obtained from the intensities of the diffracted beams. From equation (41) it can be seen that the Patterson function will attain large values only if the vector defined by (uvw) corresponds to a vector between two peaks in the electron density distribution; the value of P(uvw) will then be approximately the product of the electron density values at the two peaks.

Thus the peaks in the Patterson summation correspond to the ends of the interatomic vectors with one end at the origin. For a structure containing N atoms, it can be shown that N(N - 1) distinct peaks should be present in the Patterson function. Harker (1936) pointed out that the presence of certain elements of symmetry results in peaks being concentrated on certain lines and sections through the three dimensional Patterson function. Unfortunately for structures containing more than a very small number of atoms, there are a large number of peaks in the vector map. Overlap occurs and the peaks cannot, in general, be resolved.

However, if a heavy atom is present, it can be located since it gives rise to high vector peaks which then stand out against the background of overlapping smaller peaks due to the presence of lighter atoms in the structure. Thus the coordinates of the heavy

atom can often be obtained from the vector map by inspection. Once the position of the heavy atom is known, the remaining atoms in the structure can then be located by direct Fourier methods.

1.6.2 The Heavy Atom Method

The heavy atom method of determining the unknown phase angles associated with the known structure amplitudes depends on the presence of an atom or group of atoms of high atomic number compared with the remainder of the structure. Since the diffraction of X-radiation is dependent on the electron density of the atoms, the heavy atom will dominate the diffracted spectra. Thus the contribution of the heavy atom to the structure factors will outweigh that of the light atoms.

If the position of the heavy atom can be determined, either from a consideration of the Patterson function or by space group symmetry, a phase angle which will approximate to the phase angle of the complete structure may then be calculated for each structure amplitude. The electron density distribution may then be evaluated by summation of the appropriate Fourier series, using the calculated phase angles and the observed structure amplitudes, and further features of the molecule may be resolved. It is then possible to derive the complete molecular structure by an

iterative process of improving the phase angles by including the light atoms in the structure factor calculation and then evaluating the resultant electron density distribution. The main disadvantage of this method is that the major part of the structure amplitude comes from the scattering of the heavy atom and the accuracy with which the positions of the remaining lighter atoms can be fixed is correspondingly lessened.

This difficulty may be minimised in the method of isomorphous substitution. In this method of phase angle determination at least one heavy atom derivative isomorphous with the parent compound in the case of centrosymmetric structures and two heavy atom derivatives in the case of non-centrosymmetric structures must be available. Since the replacement of an atom in the parent compound by a heavier atom will give rise to differences in the intensities of the diffracted beams, and therefore in the structure amplitudes of the two isomorphs, the heavy atom need not dominate the scattering as in the case of the heavy atom method. If the position of the heavy atom is known, its contribution to the structure factors can be calculated and the phase angles associated with the diffracted spectra may be derived. The resultant refinement may then be carried out on an isomorphous derivative in which the heavy atom has been replaced by a lighter one. The main disadvantage of the method is in the condition of strict isomorphism which must be imposed.

The structural studies of the phthalocyanines by Robertson, (1935; 1936) and Robertson and Woodward, (1937; 1940) are classical examples of the successful application of both heavy atom and isomorphous substitution methods.

1.6.3 Direct Methods

Although the solution of any unknown structure by the heavy atom method or by means of the Patterson function is a direct solution, the term "direct method" has been restricted by usage to methods which attempt to obtain phase information from the measured structure amplitudes.

The first direct method of structure solution was based on inequality relationships which arise between the structure amplitudes when the electron density is restricted to positive values (Harker and Kasper, 1948). Further development of direct methods was due to Sayre, (1952) who derived equality relationships between the structure amplitudes.

Karle and Hauptman, (1952; 1953; 1954) formulated a statistical treatment which can yield information about the phase angles. They developed mathematical relationships involving normalised structure factors defined as

$$E = \frac{1}{(\langle \overline{F^2} \rangle)^{1/2}} . F \qquad (46)$$

where E is the normalised structure factor and $\langle \overline{F^2} \rangle$ is the "local average" value of F^2. In their "symbolic addition" method, letter phases are assigned to various large E values. Phase angle determination is usually based on the Karle and Hauptman Σ_2 relationship which is similar to Sayre's equation. This method has found wide use in the case of centrosymmetric structures and non-centrosymmetric structures which contain centrosymmetric projections, (Karle and Karle, 1968).

1.7 Methods of Structure Refinement

In the initial stages of a crystal structure analysis, the approximate electron density syntheses obtained generally yield the positions of most atoms in the structure. In the process of structure refinement some function of the difference between the observed structure amplitudes and those calculated for the model which is being refined is minimised. The usual function minimised is the residual or R-factor which is defined by

$$R = \sum \left| |F_o| - |F_c| \right| / \sum |F_o| \qquad (47)$$

where $|F_o|$ is the observed structure amplitude, $|F_c|$ is that calculated for the model and the summation is over the structure amplitudes used in the refinement. The value attained by R may be taken as a measure of the correctness of the proposed model.

1.7.1 Fourier Refinement Methods

The atomic positions obtained from an approximate electron density synthesis may be used to compute phases which are closer to the true values than those on which the original synthesis was based. It is therefore possible, by preparing successive electron density syntheses, to calculate continually better approximations to the true phases. Such a process of refinement is complete when the phases derived from a synthesis are the same as those used to

calculate it.

The chief advantage of this method of refinement is that it can be initiated before all the atoms in the structure have been located. The main disadvantage of the Fourier method is that the atomic positions derived from it are affected by termination of series errors. This is due to experimental limitations in that it is necessary to truncate the Fourier series used to calculate the electron density distribution after a finite number of terms.

Booth (1946) has suggested a method, known as the backshift correction, for dealing with this effect. In this method two separate electron density maps are computed using the calculated and measured structure factors as coefficients in each case. Both maps will be subject to the same termination of series errors and the atomic coordinates will therefore be similarly affected in both cases. In the case of the F_c synthesis, however, specific coordinates were used in the calculation and the positions derived from the map would be unaltered but for the presence of termination of series errors. The corrected atomic coordinates may then be derived by subtracting the differences between the coordinates used to calculate the F_c map and those derived from it from the coordinates derived from the F_o map.

The properties of the difference synthesis, which is derived from a Fourier series whose coefficients are $(F_o - F_c)$, have been

described by Booth (1948a; 1948b) and by Cochran (1951). The difference synthesis of a completely refined structure has a flat topography in which only random fluctuations in density are apparent. Errors in atomic coordinates and thermal parameters may therefore be detected and corrected by the use of difference syntheses. The main applications of the difference synthesis in structure analysis have been in determining the positions of hydrogen atoms and in ensuring that the refinement of a structure is complete.

1.7.2 Least-squares Refinement

The first application of the least-squares method to crystal structure analysis was given by Hughes (1941). The object of structure refinement is to minimise some function of the differences between the observed and calculated structure amplitudes with respect to the structure parameters. In the least-squares procedure the function normally minimised is

$$M = \sum_m w(|F_o| - |F_c|)^2 = \sum_m w\Delta^2 \qquad (48)$$

where the summation is over all m independent structure amplitudes and w is the weight chosen to reflect the accuracy of the observations. If the standard deviation of $F_o(hkl)$ is $\sigma(hkl)$,

it can be shown that the weight which gives the lowest standard deviations in the derived parameters is

$$w(hkl) = 1/\sigma^{-2}(hkl) \tag{49}$$

Normally only relative weights which depend on some function of $|F_o|$ are used.

If $p_1, p_2, \ldots, p_n$ are the n parameters whose values are to be determined from F_c, then the condition that M is a minimum is given by

$$\partial M/\partial p_j = 0 \qquad (j = 1,2,\ldots,n) \tag{50}$$

$$\text{i.e. } \sum w\Delta\partial|F_c|/\partial p_j = 0 \tag{51}$$

for a trial set of p_j close to the correct values, Δ may be expanded as a function of the parameters by a first order Taylor series

$$\Delta(\underline{p} + \underline{e}) = \Delta(\underline{p}) - \sum_{i=1}^{n} e_i \partial|F_c|/\partial p_i \tag{52}$$

where e_i is the required small change in the parameter p_i and $\underline{p}$ and $\underline{e}$ represent the complete set of parameters and changes.

Substitution of (52) in (51) yields the normal equations

$$\sum_{i=1}^{n}\left\{\sum_{m} w\partial|F_c|/\partial p_i \cdot \partial|F_c|/\partial p_j\right\} e_i = \sum_{m} w\Delta\partial|F_c|/\partial p_j \qquad (53)$$

There are, therefore, n equations in n unknowns which must be solved for the corrections e_i in the individual parameters.

The normal equations may be written in matrix notation as

$$\sum_{i=1}^{n} a_{ij} \cdot e_i = b_j \qquad (54)$$

where

$$a_{ij} = \sum_{m} w\partial|F_c|/\partial p_i \cdot \partial|F_c|/\partial p_j \qquad (55)$$

and

$$b_j = \sum_{m} w\Delta\partial|F_c|/\partial p_j \qquad (56)$$

The solution of (54) is given by

$$e_i = \sum_{i=1}^{n} (a^{-1})_{ij} \cdot b_j \qquad (57)$$

where $(a^{-1})_{ij}$ is the inverse matrix of a_{ij}.

Due to the limitation of the expansion of Δ as a Taylor series (52) to two terms, it is necessary to calculate several cycles of refinement before convergence is obtained. The criterion generally used to decide when a refinement should be terminated is

that the ratio of the shift e_i of each parameter to its standard deviation should be less than unity. The course of the refinement may be followed from the residual defined by equation (47) or from the modified residual

$$R' = \sum w\Delta^2 / \sum w|F_o|^2 \qquad (58)$$

The main disadvantage of the modified residual is that it may be affected by changes in the weighting scheme.

1.8 The Accuracy of Results

At the conclusion of a crystal structure analysis it may be necessary to have some assessment of the accuracy with which the refined parameters have been determined so that useful comparisons with theoretical predictions and other experimental observations may be made. The accuracy of the refined parameters may be derived from their estimated standard deviation (σ).

The variance $\sigma^2(p_i)$ of the parameter p_i is given by

$$\sigma^2(p_i) = (a^{-1})_{ii} \sum w\Delta^2/(m - n) \qquad (59)$$

where m is the number of observations and n is the number of parameters defining the structure and $(a^{-1})_{ii}$ is the diagonal element of the inverse matrix of the normal equations. The covariance of the parameters p_i and p_j is given by

$$\begin{aligned} \mathrm{cov}(p_i,p_j) &= (a^{-1})_{ij} \sum w\Delta^2/(m - n) \\ &= \sigma^2(p_i).\sigma^2(p_j).r_{ij} \end{aligned} \qquad (60)$$

where r_{ij} is the correlation coefficient between the parameters. The above equations are, however, only valid if the weighting scheme is appropriate to the data. The standard deviations of functions of the refined parameters may be estimated from the

parameter variances and covariances obtained from equations (59) and (60) by the application of statistical methods.

If x is the value of an experimentally derived quantity whose standard deviation is s(x), based on n degrees of freedom, the probability P that x differs significantly from its theoretical value p due to random experimental errors is given by t, where t is a random variable distributed in Student's distribution with n degrees of freedom, and defined by

$$t = |x - p|/s(x) \tag{61}$$

When n is large, as is normal in crystal structure analysis, the distribution is normal and t = 2.6 for P = 1% and t = 3.3 for P = 0.1%. If $2.6 < t < 3.3$, the difference probably does not arise from random errors.

If the agreement between a set of experimental results and their expected values is under consideration, the χ^2 test may be applied . If, d_i is the deviation of the i^{th} member of a set of n points, then

$$\chi^2 = \sum_{i=1}^{n} d_i^2/\sigma^2 \tag{62}$$

where σ is the average standard deviation in the positional parameter of the point. The probability that the deviation is due

to random experimental errors can be found from tables of the χ^2 distribution for n-3 degrees of freedom, (Fisher and Yates, 1953).

PART II

CRYSTAL STRUCTURE ANALYSES

OF

CLATHRATES

Introduction

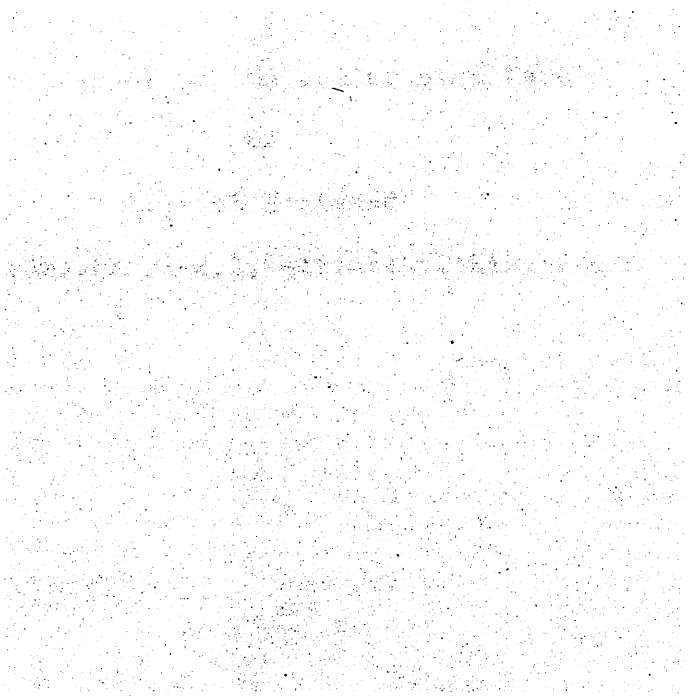
In a clathrate, the molecules of the host component are linked together so as to leave cages in which one, or more, molecules of the guest component may be accommodated. Clathrates can be classified according to the nature of the forces linking their host molecules; these may be hydrogen bonds as in β- quinol (Palin and Powell, 1947) or van der Waals' forces as in tri-o-thymotide (Lawton and Powell, 1958). Phenol (von Stackelberg et al., 1958) and Dianin's and related compounds (MacNicol et al., 1969; Flippen et al., 1970) are of an intermediate type using both hydrogen bonds and van der Waals' forces.

The first organic clathrate to be discovered was the hydrogen sulphide included form of quinol by Wohler, (1849). Subsequent investigations showed that quinol formed a series of complexes with organic molecules of moderate dimensions. It is interesting to note that Mylius, (1886) concluded that no chemical combination existed between the components of the complex but that the quinol molecules were somehow able to lock the guest component in position.

Early X-ray investigations of the related inclusion compounds formed by deoxycholic acid proved inconclusive (Giacomello and Kratsky, 1936; Giacomello, 1943). Although the general orientation

of the host molecules forming the cavity was defined, atomic resolution was not obtained. Subsequent investigations, however, appear to confirm Kratsky and Giacomello's predicted structure (Damiani et al., 1967).

The true nature of the complexes formed by quinol and related systems was finally established by the classic work of Powell on the clathrates formed by β- quinol.

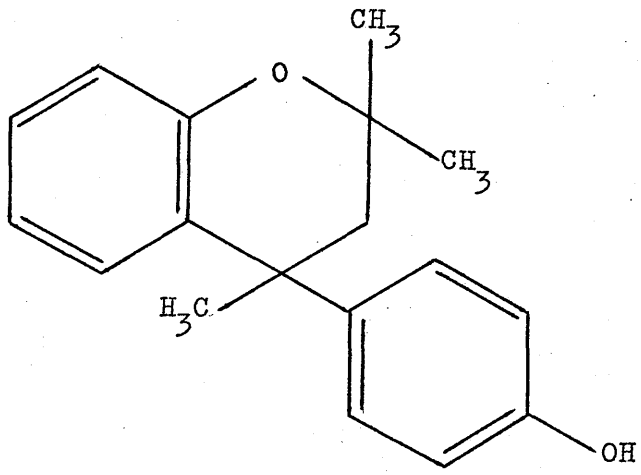


Chapter 1

The Crystal and Molecular Structure of Ethanol Included 4-*p*-Hydroxyphenyl-2,2,4-trimethylthiachroman

1.1 Introduction

Dianin, (1914) found that phenol and mesityl oxide condense in the presence of hydrogen chloride to form a monohydric phenol (I).



(I)

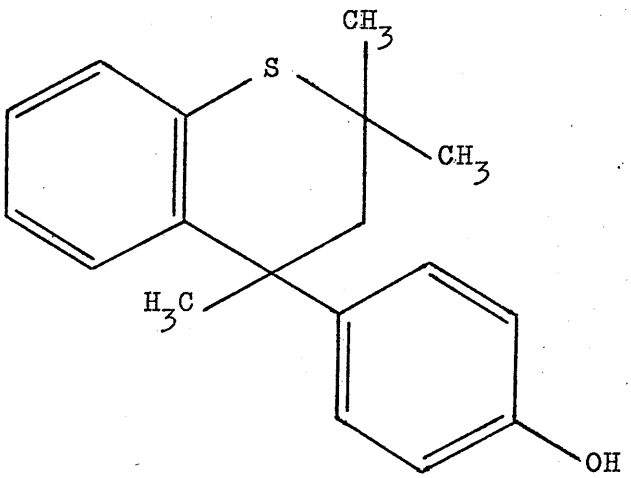
It was found that (I) formed crystalline inclusion compounds with a variety of substances. Dianin noted that the different adducts of (I) had similar crystalline forms.

In the course of investigations into the condensation reactions of phenols, Baker et al., (1955) re-investigated Dianin's compound. The correct formula of (I) was established by Baker. In the course of this work it was found that Dianin's compound formed a greater variety of crystalline inclusion compounds than any other known organic compound. The host-guest ratio of the various adducts was shown on analysis to be greater than or equal to 3:1 or 6:1 in every case.

On the basis of goniometric and X-ray studies, Powell and Wetters, (1955) found that the various adducts have similar crystalline forms and suggested that they were clathrates. Several of the adducts were found to have approximately the same unit cell dimensions which, referred to hexagonal axes, were $\underline{a} \sim 27.0$ and $\underline{c} \sim 11.1$ Å. The unit cell contained 18 molecules of (I) and the space group was either R3 or $R\bar{3}$. If the space group is $R\bar{3}$, then any molecule is in one of a group of six equivalent positions related by a three-fold inversion axis, $\bar{3}$. Powell suggested that the hydroxy groups should be joined by hydrogen bonds, thus linking the six equivalent molecules in a hexagon of side approximately 2.8 Å similar to that found in the β - quinol (Palin and Powell, 1947) and phenol (von Stackelberg et al., 1958) clathrates which have the same space group symmetry. The hexagon of hydrogen bonded hydroxy groups would then form a waist from which alternate molecules point up or down so that three form an upper and three a lower cup-like structure. In the crystal these groups are directly above one another with their symmetry axis parallel to the $\underline{c}$ - axis, thus leaving cavities, within which guest molecules may be accommodated.

Although the molecular structure of Dianin's compound had been unambiguously established by synthesis (Baker et al., 1956a), initial attempts to modify the basic host molecule whilst still

retaining the clathrating property proved unsuccessful (Baker et al., 1956b). However MacNicol, (1969) synthesised the thia-analogue (II) of Dianin's compound.



(II)

The thiachroman (II) formed clathrates with a variety of solvents which were isomorphous with those formed by Dianin's compound.

Subsequent structural analyses of (I) by Flippen et al., (1970) and of (II) by MacNicol et al., (1969) succeeded in showing that the structure of Dianin's compound was closely related to that originally proposed by Powell.

1.2 Experimental

Crystal Data

Host: 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman

Guest: ethanol

Host:Guest :: 3:1

3 $C_{18}H_{20}OS$: C_2H_6O . F.W. = 299.8

Trigonal, a = 27.81 Å, c = 10.90 Å, (referred to hexagonal axes)

U = 7299 $Å^3$ F(000) = 2892 electrons

D_m = 1.22 $g.cm.^{-3}$ Z = 18 D_x = 1.227 $g.cm.^{-3}$

Space group: $R\bar{3}$ (C_{3i}^2, No. 148)

Linear absorption coefficient (Cu K_α, λ = 1.5418 Å) = 17 $cm.^{-1}$

The crystals used in this analysis were supplied by Dr. D.D. MacNicol. They consisted of colourless hexagonal needles elongated along the c-axis. Unit cell dimensions were obtained from rotation and Weissenberg photographs (Cu K_α radiation, λ = 1.5418 Å) taken about the c-axis. From the systematically absent spectra, the space group is either R3 (No. 147) or $R\bar{3}$ (No. 148). The centrosymmetric space group ($R\bar{3}$) was chosen and this choice has been justified by the success of the subsequent analysis.

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the hki0,...hki9

reciprocal lattice nets taken with Cu K_α radiation. The multiple film technique of Robertson, (1943) with six films per pack was used. The observed intensities were reduced to structure amplitudes by applying the appropriate Lorentz, polarisation and rotation factors (Tunell, 1939). 2272 independent structure amplitudes (Table 1.4) were obtained, which represents 61 % of the data accessible to Cu K_α radiation. No absorption corrections were applied in the analysis.

The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

1.3 Solution and Refinement of the Structure

In the space group $R\bar{3}$, the equivalent positions are:-

$$\pm (x, y, z), \pm (-y, x-y, z), \pm (y-x, -x, z);$$

together with those generated by the R-centred Bravais lattice given by:-

$$\pm (\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3}) \pm (x, y, z),$$

$$\pm (\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3}) \pm (-y, x-y, z),$$

$$\pm (\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3}) \pm (y-x, -x, z).$$

A heavy atom situated in a general position will therefore give rise to the following set of vectors:-

$\pm (2x, 2y, 2z)$	single weight,
$\pm (-2y, 2x-2y, 2z)$	single weight,
$\pm (2y-2x, -2x, 2z)$	single weight,
$\pm (x-y, x, 2z)$	double weight,
$\pm (y, y-x, 2z)$	double weight,
$\pm (-x, -y, 2z)$	double weight,
$\pm (x+y, 2y-x, 0)$	double weight,
$\pm (2x-y, x+y, 0)$	double weight,
$\pm (x-2y, 2x-y, 0)$	double weight.

Thus in the three-dimensional Patterson summation, there are six dominant peaks. Three are in general positions and three are on the Harker section at w = 0. Any one of the three peaks on the Harker section will suffice to determine the x and y coordinates of the heavy atom, whilst the x, y and z coordinates of the heavy

atom may be obtained from any one of the three general peaks.

The asymmetric unit of the three dimensional Patterson function was calculated and interpreted on the basis of the analytical functions given. The values obtained for the coordinates of the sulphur atom were:-

ATOM	X/a	Y/b	Z/c
S(1)	0.2623	0.0770	0.6511

A set of structure factors, based on the position of the sulphur atom was calculated, and the calculated phase angles used in conjunction with the observed structure amplitudes to evaluate an electron density synthesis. The coordinates of all the remaining non-hydrogen atoms in the structure were obtained from this initial electron density synthesis. The different chemical species present in the structure were differentiated on the basis of peak height and knowledge of the chemical structure.

Inclusion of the nineteen atoms (1 oxygen and 18 carbon) in the structure factor calculation reduced the residual R from 0.58 with the heavy atom alone to 0.28. The atomic scattering factors used in the second structure factor calculation and throughout the remainder of the analysis were those of Hoerni and Ibers, (1954) for carbon and oxygen and those of Dawson, (1960) for sulphur. A second electron density distribution was evaluated using both the improved phases and observed structure amplitudes. The improved

coordinates derived from this distribution reduced the residual R to 0.249 in the resultant structure factor calculation. Coordinates derived from a third distribution reduced the residual further to 0.240.

The structure was further refined in eight cycles of minimisation of the function $M = \sum w(|F_o| - |F_c|)^2$ by the method of least-squares. The least-squares program of D.R. Pollard, (1968) was used in the initial stages of this refinement. Each reciprocal lattice net was given an individual scale factor and each atom an individual isotropic temperature factor. The observations were all given unit weight. After three cycles of full matrix least-squares refinement, the R-factor was reduced to 0.182. A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 2/|F_o|_{max}$, which has been recommended by Cruickshank, (1961) for use with photographic data, was then applied and a further cycle of least-squares refinement calculated. The residual R was reduced to 0.178.

The Glasgow S.F.L.S. program (Cruickshank and Smith, 1965) was then used to continue the refinement. Lingafelter and Donahue, (1966) have shown that, if the observations are collected up only one axis, there is insufficient information to permit the refinement

of individual layer scale factors and anisotropic thermal parameters. On the assumption that the data were on the same relative scale at the conclusion of the isotropic refinement, it was therefore decided to refine individual anisotropic thermal parameters and a single overall scale factor. As a result of allowing for the anisotropic vibrations of the atoms, a further four cycles of refinement in which the block diagonal approximation to the normal matrix was applied produced convergence. The R-factor over the 2272 independent reflections was reduced to 0.141. The weighting scheme applied in the last four cycles of refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2 + p_4|F_o|^3)$$

where $p_1 = 4.0$, $p_2 = 0.3$, $p_3 = 0.001$ and $p_4 = 0$. No shifts greater than 0.2 in atomic coordinates or thermal parameters were observed in the final cycle. The course of the refinement is summarised in Table 1.1.

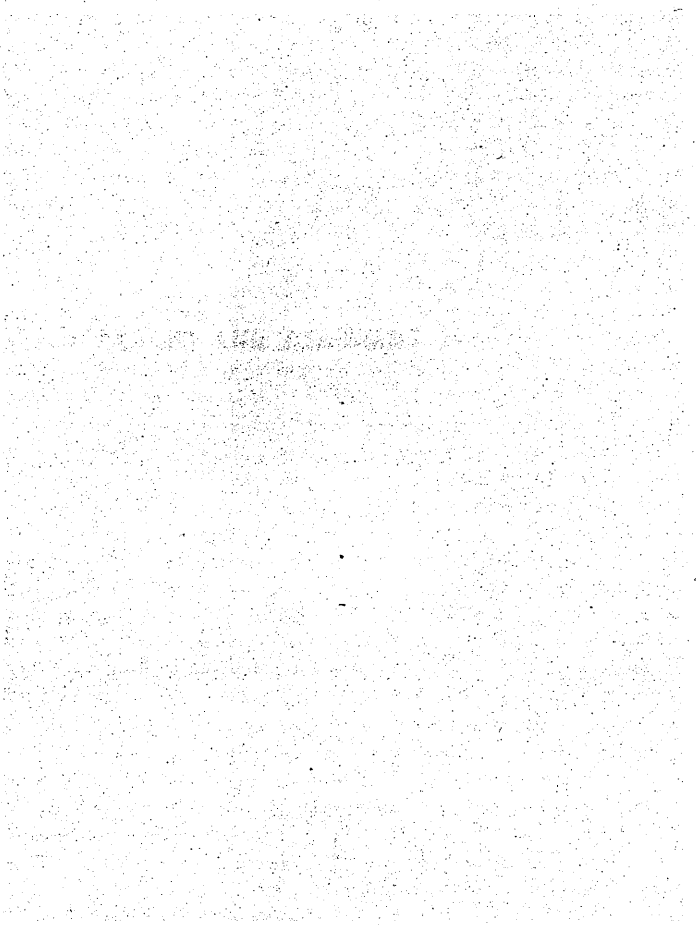
The structure factors calculated in the final cycle of least-squares refinement were used to phase a difference synthesis of the cavity. This showed a set of disordered peaks at approximately $z = 0.13$ and $z = 0.26$ together with their symmetry related partners at $z = 0.74$ and $z = 0.87$ respectively. This may indicate the presence of included ethanol molecules in this region of the cavity.

Tables 1.2 and 1.3 respectively contain the final values of

the fractional atomic coordinates and anisotropic temperature factors together with their estimated standard deviations derived from the inverse of the normal least-squares matrix. The observed and final calculated structure amplitudes are given in Table 1.4. Atomic coordinates in Angstroms referred to orthogonal axes defined by X' parallel to $\underline{a}^*$, Y' normal to $\underline{a}^*$ and $\underline{c}$ and Z parallel to $\underline{c}$ are given in Table 1.5. Tables 1.6 and 1.7 contain the covalent bond lengths and interbond angles in the structure together with their estimated standard deviations. Table 1.8 lists all intermolecular contacts between the atoms which are less than 4 Å and in Table 1.9 the equations of the molecular planes through certain portions of the molecule are given, together with the deviations of certain atoms from these planes. Estimated standard deviations, where quoted, are in units of the last decimal place of the quantity to which they refer.

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 1.1. The thiachroman residue projected along a line in the mean plane through S(1), C(4), C(9) and C(10) is shown in Fig. 1.2. The general packing of the molecules in the unit cell, as viewed down the $\underline{c}$-axis is illustrated in Fig. 1.3. In Figs. 1.4 and 1.5 the structure is shown projected on (010) illustrating the cavity. In Fig. 1.5 two molecules of (II), which lie directly above and below the cavity as viewed in

this direction, have been excluded apart from their hydroxyl oxygen atoms. A section through the van der Waals' surface of the cavity is shown in Fig. 1.6.



TABLES AND DIAGRAMS

FIGURE 1.1

A molecular drawing illustrating the numbering of the non-hydrogen atoms of the host.

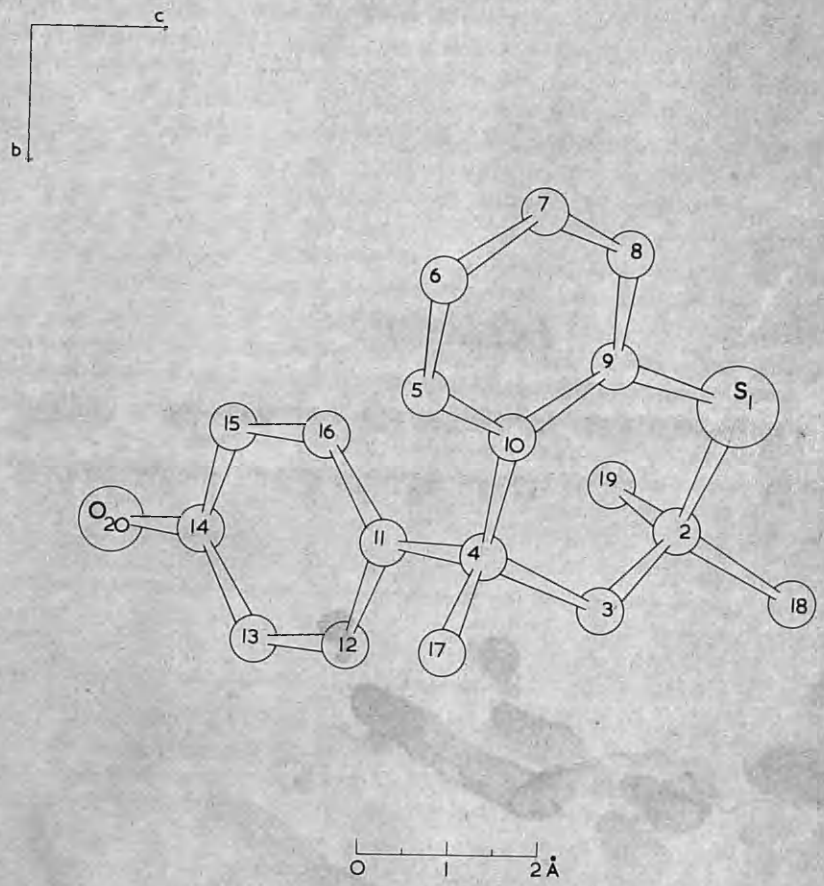

c
b
7
8
6
9
5
S1
15
16
10
19
O20
14
11
4
2
18
3
13
12
17
0
1
2 Å

FIGURE 1.2

A molecular drawing illustrating the thiachroman residue projected along a line in the mean molecular plane through S(1), C(4), C(9) and C(10).

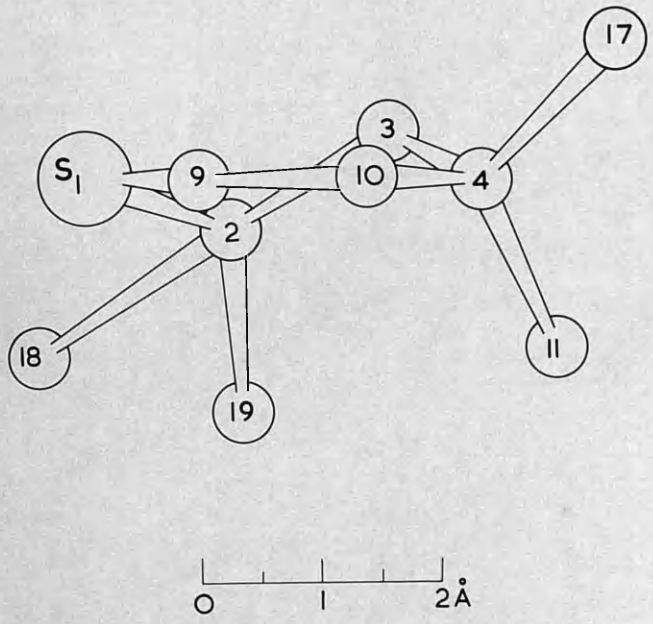

17
3
S1
9
10
4
2
18
11
19
0
1
2Å

FIGURE 1.3

The molecular packing viewed down the c-axis.

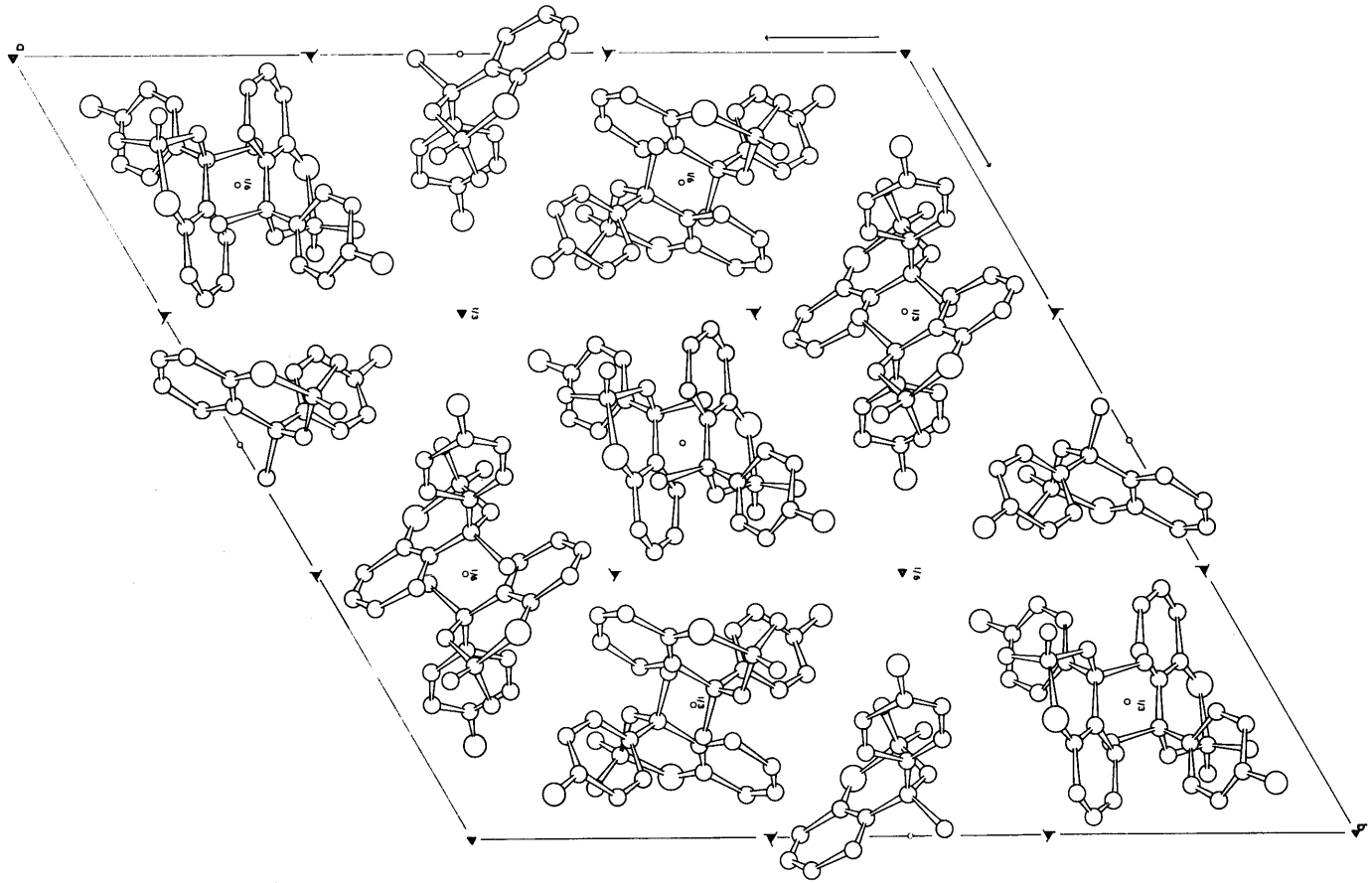


FIGURE 1.4

The packing of the molecules as projected on (010).

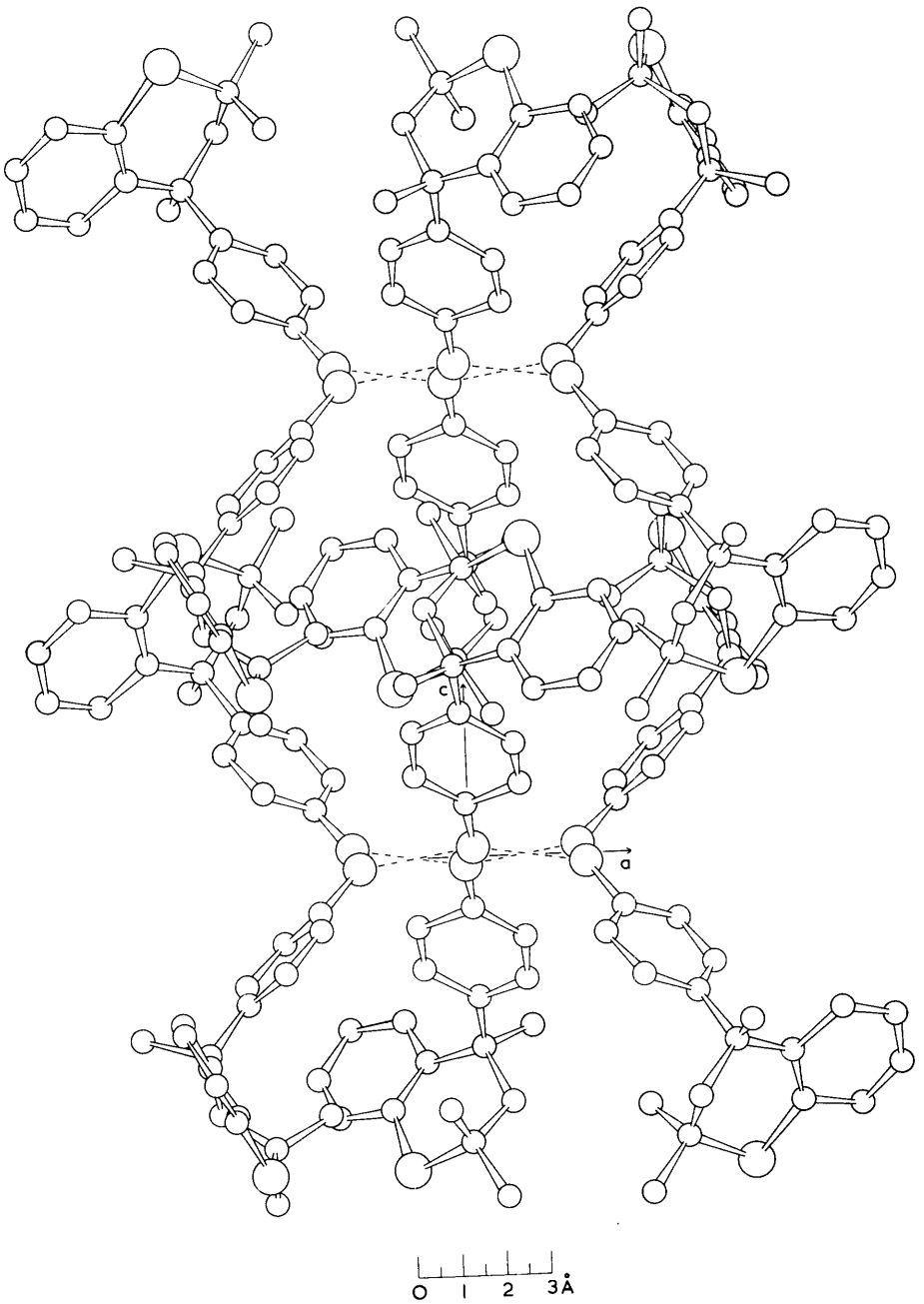
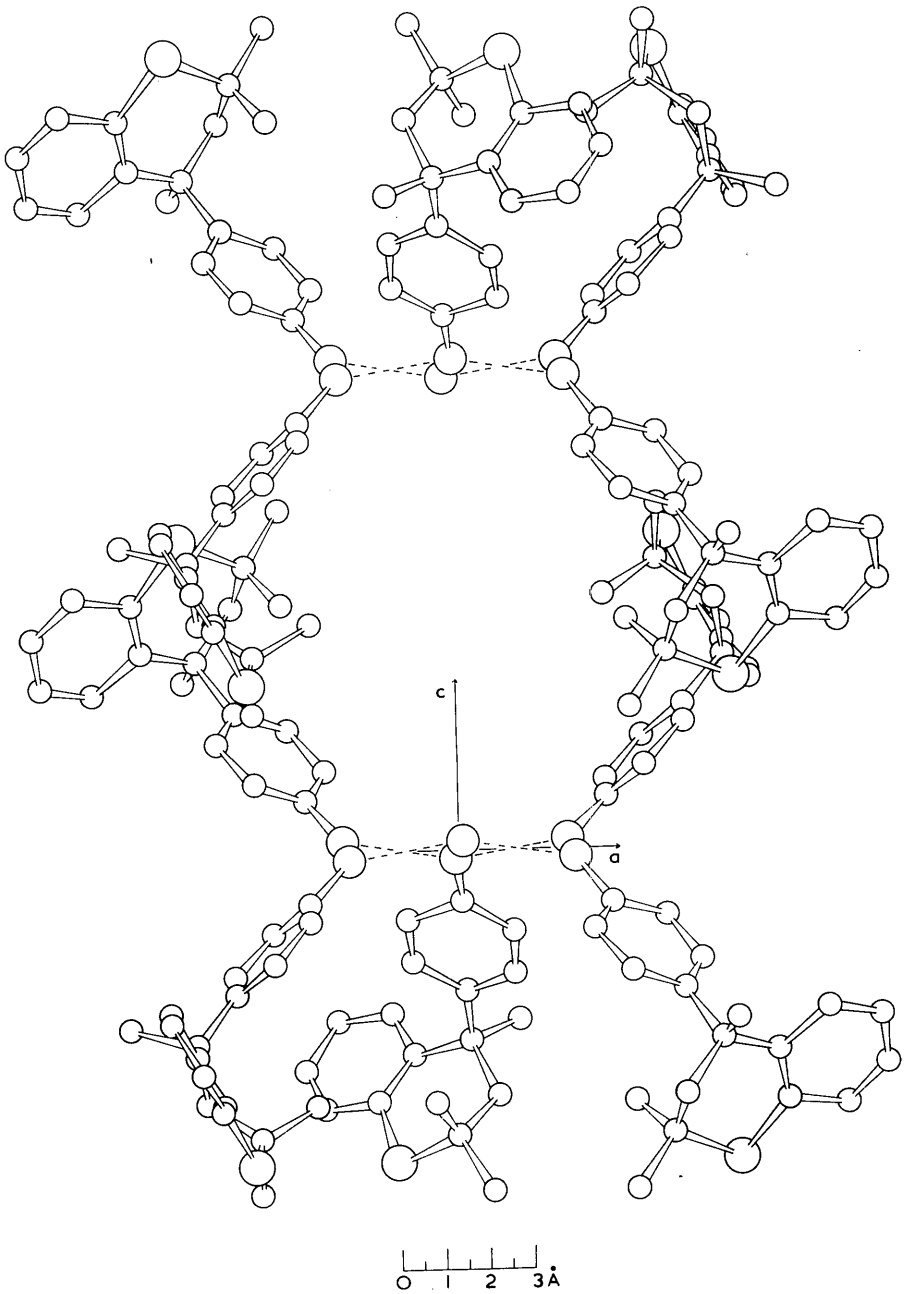

c
a
0 1 2 3Å

FIGURE 1.5

The packing of the molecules as projected on (010). Two molecules of the host, which lie directly above and below the cavity as viewed in this direction, have been excluded apart from their hydroxyl oxygen atoms.


c
a
0 1 2 3Å

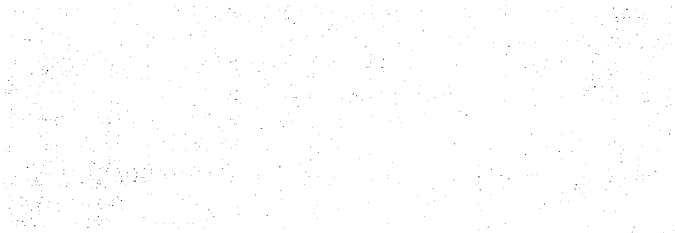
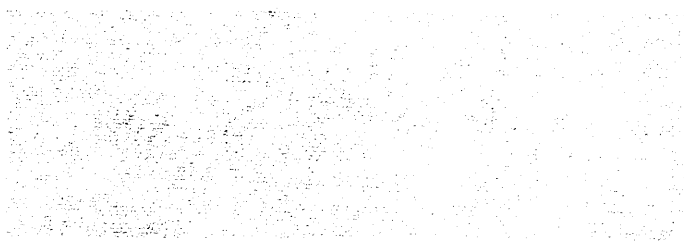


FIGURE 1.6

A section through the van der Waals' surface of the cavity.



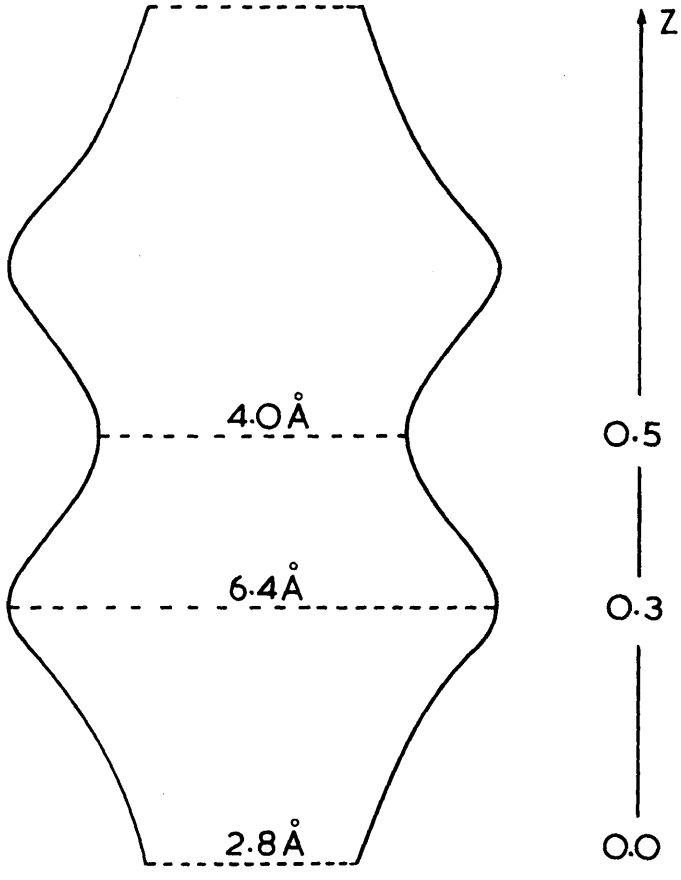

Z
4.0Å
6.4Å
2.8Å
0.5
0.3
0.0

TABLE 1.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	S	0.58
2	S + 18 C + O	0.283
3	S + 18 C + O	0.249
4	S + 18 C + O	0.240

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layer scales, unit weights	0.191
2	"	0.183
3	"	0.182
4	As above, weighting scheme 1 applied	0.178
5	Block diagonal, individual anisotropic temperature factors, weighting scheme 2 applied	0.166
6	"	0.145
7	"	0.142
8	"	0.141

TABLE 1.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
S(1)	0.2624 ± 1	0.0771 ± 1	0.6508 ± 1
C(2)	0.2205 ± 2	0.1061 ± 2	0.5928 ± 5
C(3)	0.2590 ± 2	0.1578 ± 2	0.5179 ± 5
C(4)	0.2854 ± 2	0.1503 ± 2	0.3978 ± 4
C(5)	0.3536 ± 2	0.1199 ± 3	0.3351 ± 6
C(6)	0.3806 ± 3	0.0892 ± 3	0.3511 ± 6
C(7)	0.3699 ± 2	0.0557 ± 3	0.4511 ± 6
C(8)	0.3329 ± 2	0.0534 ± 2	0.5390 ± 5
C(9)	0.3050 ± 2	0.0836 ± 2	0.5267 ± 5
C(10)	0.3137 ± 2	0.1168 ± 2	0.4241 ± 5
C(11)	0.2422 ± 2	0.1239 ± 2	0.2965 ± 4
C(12)	0.2129 ± 2	0.1502 ± 2	0.2592 ± 5
C(13)	0.1726 ± 2	0.1281 ± 2	0.1664 ± 5
C(14)	0.1608 ± 2	0.0792 ± 2	0.1113 ± 5
C(15)	0.1901 ± 2	0.0532 ± 2	0.1413 ± 5
C(16)	0.2304 ± 2	0.0753 ± 2	0.2347 ± 4
C(17)	0.3293 ± 2	0.2103 ± 2	0.3588 ± 5
C(18)	0.2037 ± 3	0.1257 ± 3	0.7108 ± 6
C(19)	0.1700 ± 2	0.0631 ± 2	0.5256 ± 5
O(20)	0.1212 ± 2	0.0560 ± 2	0.0201 ± 4

TABLE 1.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
S(1)	0.0484 6	0.0527 6	0.0410 9	0.0260 10	0.0101 9	0.0501 10
C(2)	0.0484 24	0.0400 21	0.0433 31	0.0010 36	0.0043 38	0.0429 38
C(3)	0.0519 25	0.0402 21	0.0404 31	0.0003 35	0.0019 38	0.0553 39
C(4)	0.0409 20	0.0311 18	0.0372 28	0.0001 31	0.0039 33	0.0356 32
C(5)	0.0499 27	0.0720 34	0.0521 37	-0.0100 51	0.0015 45	0.0716 51
C(6)	0.0623 32	0.0786 37	0.0439 36	-0.0136 52	-0.0048 49	0.0888 59
C(7)	0.0551 28	0.0634 30	0.0585 38	-0.0243 51	-0.0276 48	0.0756 49
C(8)	0.0561 28	0.0587 28	0.0504 35	0.0034 46	-0.0131 46	0.0711 49
C(9)	0.0365 20	0.0397 21	0.0394 30	0.0017 33	-0.0082 34	0.0315 34
C(10)	0.0404 21	0.0433 22	0.0388 28	-0.0021 35	-0.0045 36	0.0445 37
C(11)	0.0429 21	0.0325 18	0.0317 26	0.0043 30	-0.0036 32	0.0339 32
C(12)	0.0531 25	0.0442 23	0.0408 31	-0.0060 37	-0.0116 39	0.0561 41
C(13)	0.0542 26	0.0520 25	0.0422 30	0.0030 40	0.0003 40	0.0707 44

C(14)	0.0440 22	0.0470 24	0.0379 30	-0.0105 37	-0.0130 36	0.0453 38
C(15)	0.0490 24	0.0420 22	0.0408 31	-0.0056 37	-0.0013 38	0.0476 38
C(16)	0.0447 21	0.0405 20	0.0275 26	-0.0034 30	0.0018 32	0.0504 34
C(17)	0.0475 25	0.0407 24	0.0460 34	0.0056 39	-0.0061 41	0.0233 39
C(18)	0.0758 38	0.0624 32	0.0446 37	-0.0003 48	0.0162 53	0.0689 58
C(19)	0.0400 23	0.0457 24	0.0498 33	-0.0006 41	0.0002 41	0.0169 39
O(20)	0.0592 21	0.0612 21	0.0429 23	-0.0103 32	-0.0215 31	0.0669 36

TABLE 1.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES

H	K	L	F OBS	F CALC
4	1	0	37.2	42.9
7	1	0	136.3	140.8
10	1	0	158.0	158.9
16	1	0	84.3	81.2
19	1	0	39.5	29.4
22	1	0	49.0	44.9
25	1	0	8.2	15.8
2	2	0	128.5	127.2
5	2	0	115.7	113.2
8	2	0	105.6	102.9
11	2	0	15.2	1.9
14	2	0	4.7	3.5
20	2	0	15.4	13.4
29	2	0	17.1	18.7
0	3	0	306.4	319.6
3	3	0	272.1	273.7
6	3	0	103.3	100.8
9	3	0	22.7	22.4
12	3	0	82.8	77.4
15	3	0	30.3	31.4
18	3	0	31.3	31.2
21	3	0	59.9	60.6
24	3	0	34.8	37.6
27	3	0	24.6	29.6
1	4	0	218.7	237.5
4	4	0	25.5	27.8
7	4	0	110.6	114.3
10	4	0	90.6	96.0
13	4	0	131.5	136.1
19	4	0	59.8	62.4
22	4	0	54.2	59.6
28	4	0	11.6	15.3
2	5	0	169.5	167.1
11	5	0	46.5	49.0
14	5	0	33.8	25.5
17	5	0	37.0	30.8
20	5	0	40.6	37.6
23	5	0	8.1	11.5
26	5	0	38.6	36.8
0	6	0	235.1	253.1
3	6	0	36.8	31.2
6	6	0	45.7	46.2
9	6	0	23.6	16.0
15	6	0	39.2	42.4
18	6	0	23.6	18.7
24	6	0	22.9	17.9
27	6	0	9.8	12.1
1	7	0	34.0	32.3
4	7	0	142.5	138.1
7	7	0	30.4	37.3
10	7	0	37.3	37.1
16	7	0	21.6	21.1
19	7	0	15.4	13.3
25	7	0	33.9	30.7
28	7	0	168.2	169.4
5	8	0	130.2	123.1
8	8	0	19.3	18.7
11	8	0	61.6	55.7
14	8	0	12.1	14.6
17	8	0	34.7	34.1
20	8	0	62.1	56.8
23	8	0	12.0	14.8
26	8	0	8.4	10.9
0	9	0	65.0	72.7
3	9	0	87.1	81.0
6	9	0	27.8	27.5
9	9	0	161.9	161.2
12	9	0	38.1	29.2
15	9	0	8.9	10.2
18	9	0	15.2	8.4
21	9	0	17.2	14.9
24	9	0	16.5	16.2
1	10	0	92.5	87.7
4	10	0	61.0	58.7
7	10	0	79.1	70.3
13	10	0	86.9	79.0
16	10	0	23.6	24.4
19	10	0	20.2	19.2
2	11	0	104.6	105.7
11	11	0	57.2	65.0
14	11	0	36.9	30.6
17	11	0	29.9	31.1
23	11	0	11.1	15.4
0	12	0	48.9	38.0
3	12	0	44.2	39.3
6	12	0	91.4	83.4
9	12	0	90.4	83.3
12	12	0	50.6	52.2
1	13	0	6.7	1.1
4	13	0	82.3	77.3
7	13	0	72.6	67.9
10	13	0	21.4	23.1
13	13	0	26.3	24.8
16	13	0	16.8	14.9
19	13	0	44.3	40.5
22	13	0	15.2	17.0
2	14	0	34.8	29.7
5	14	0	67.3	54.8
11	14	0	41.0	32.1
20	14	0	19.7	8.0
0	15	0	99.4	97.6
3	15	0	13.5	10.2
6	15	0	62.0	62.1
9	15	0	68.0	61.2
12	15	0	30.6	27.5
7	16	0	15.3	11.4
10	16	0	51.3	44.6
13	16	0	27.8	28.4
19	16	0	4.5	2.7
2	17	0	52.9	47.4
8	17	0	21.9	20.1
11	17	0	32.6	29.2
14	17	0	7.5	4.8
0	18	0	24.7	26.9
3	18	0	30.0	27.9
6	18	0	36.9	25.3
9	18	0	49.6	52.6
12	18	0	7.9	6.5
1	19	0	38.6	35.1
4	19	0	33.4	24.5
7	19	0	33.2	34.2
10	19	0	40.4	42.5
13	19	0	21.9	27.5
16	19	0	9.1	12.3
2	20	0	29.5	32.2
8	20	0	49.3	42.7
11	20	0	7.3	9.4
H	K	L	F OBS	F CALC
14	20	0	9.5	11.4
0	21	0	59.6	50.0
6	21	0	8.6	3.6
12	21	0	14.9	15.3
1	22	0	60.0	55.2
4	22	0	19.4	14.7
10	22	0	17.4	21.6
13	22	0	19.9	25.7
5	23	0	66.7	63.0
11	23	0	21.0	23.6
6	24	0	21.5	25.4
9	24	0	23.4	29.4
1	25	0	8.2	6.7
4	25	0	20.5	20.7
7	25	0	19.7	25.2
1	26	0	12.9	15.8
4	26	0	16.6	23.2
6	27	0	19.7	25.2
1	28	0	12.9	15.8
4	28	0	20.6	20.4
2	29	0	21.0	24.8
0	30	0	23.0	20.7
4	0	1	197.3	171.0
7	0	1	64.9	73.5
10	0	1	13.5	9.3
13	0	1	83.5	86.7
16	0	1	43.4	43.3
19	0	1	96.2	52.5
22	0	1	13.9	17.5
25	0	1	20.6	20.4
2	1	1	133.2	134.6
5	1	1	87.1	82.9
11	1	1	19.8	28.7
14	1	1	30.2	26.0
17	1	1	17.8	13.3
20	1	1	30.7	26.1
23	1	1	44.3	37.0
26	1	1	20.7	22.5
3	2	1	322.6	332.9
6	2	1	117.6	115.0
9	2	1	44.7	41.8
12	2	1	88.3	93.3
15	2	1	41.1	42.9
18	2	1	39.8	37.0
21	2	1	32.6	23.4
24	2	1	31.9	34.4
1	3	1	101.2	103.0
4	3	1	339.8	353.0
7	3	1	8.7	0.4
10	3	1	61.4	67.3
13	3	1	73.4	73.6
16	3	1	38.0	32.3
19	3	1	95.0	86.7
22	3	1	354.6	369.2
5	4	1	136.9	132.6
8	4	1	139.0	135.1
11	4	1	76.6	73.9
14	4	1	120.6	119.8
17	4	1	21.9	20.7
20	4	1	120.3	121.7
23	4	1	142.9	138.7
26	4	1	129.2	115.2
0	5	1	111.3	99.9
3	5	1	71.1	63.1
6	5	1	38.5	40.2
9	5	1	41.4	44.5
12	5	1	13.6	6.8
15	5	1	25.8	28.2
18	5	1	35.1	30.8
21	5	1	37.1	45.0
24	5	1	102.5	109.6
27	5	1	39.4	40.6
2	6	1	39.7	38.7
5	6	1	40.5	45.2
8	6	1	17.0	18.5
11	6	1	54.0	49.4
14	6	1	45.1	50.6
17	6	1	37.1	49.5
20	6	1	83.5	77.0
23	6	1	37.9	42.2
26	6	1	22.6	33.6
1	7	1	36.7	33.1
4	7	1	34.2	35.8
7	7	1	20.6	28.7
10	7	1	227.7	211.7
13	7	1	44.5	44.8
16	7	1	43.1	43.7
19	7	1	57.9	53.8
22	7	1	32.3	32.8
25	7	1	117.6	116.0
28	7	1	92.5	94.9
5	8	1	29.2	25.5
8	8	1	8.5	7.7
11	8	1	18.8	22.3
14	8	1	56.4	55.3
17	8	1	75.1	82.9
20	8	1	107.9	110.3
23	8	1	104.9	104.4
26	8	1	9.6	7.2
1	9	1	24.1	22.4
4	9	1	57.9	62.0
7	9	1	202.1	201.3
10	9	1	36.4	32.2
13	9	1	19.8	20.2
16	9	1	31.8	32.8
2	10	1	22.2	5.4
8	10	1	42.3	39.0
11	10	1	109.1	99.3
14	10	1	148.7	147.7
17	10	1	43.4	35.9
20	10	1	21.4	26.3
23	10	1	136.8	134.4
26	10	1	7.0	6.4
1	11	1	24.3	25.0
4	11	1	19.6	15.2
10	11	1	14.2	17.3
H	K	L	F OBS	F CALC
13	11	1	27.3	24.5
16	11	1	34.6	28.7
19	11	1	27.3	28.8
2	12	1	9.0	3.1
5	12	1	18.6	22.4
11	12	1	71.2	67.4
14	12	1	25.7	30.7
23	12	1	10.6	1.2
0	13	1	3.8	6.8
3	13	1	18.2	12.7
6	13	1	24.2	27.9
12	13	1	41.9	40.1
18	13	1	16.7	17.8
21	13	1	12.5	11.4
1	14	1	44.1	37.0
4	14	1	26.6	28.5
10	14	1	41.7	35.1
13	14	1	41.1	38.5
2	15	1	100.7	94.4
5	15	1	41.8	34.6
8	15	1	60.5	68.8
11	15	1	20.3	20.3
17	15	1	19.6	18.2
20	15	1	19.4	19.0
0	16	1	15.8	6.2
6	16	1	75.8	69.4
9	16	1	28.9	24.4
12	16	1	23.1	24.4
15	16	1	22.8	25.2
4	17	1	28.0	23.4
7	17	1	82.2	69.7
13	17	1	8.0	6.5
16	17	1	19.7	20.5
1	18	1	35.0	38.1
4	18	1	22.1	26.1
7	18	1	9.7	6.2
0	19	1	79.1	64.9
3	19	1	35.2	34.4
6	19	1	22.3	22.1
9	19	1	36.4	31.5
12	19	1	20.9	22.9
1	20	1	30.4	25.2
4	20	1	9.1	7.2
7	20	1	15.2	6.4
10	20	1	35.6	35.7
13	20	1	16.0	17.4
16	20	1	41.8	38.5
5	21	1	16.4	11.6
8	21	1	47.5	43.0
11	21	1	6.6	9.2
14	21	1	35.4	25.4
17	21	1	46.2	47.6
20	21	1	28.6	25.9
1	22	1	27.4	30.7
4	22	1	20.5	16.1
7	22	1	39.1	37.2
10	22	1	14.7	12.4
13	22	1	29.7	29.6
16	22	1	29.2	27.0
2	23	1	30.6	24.1
5	23	1	16.4	17.6
8	23	1	17.3	21.2
11	23	1	41.9	36.6
14	23	1	35.6	25.4
17	23	1	20.2	29.4
0	24	1	17.9	13.9
3	24	1	10.1	19.1
6	24	1	10.7	7.3
12	24	1	284.0	288.0
15	24	1	167.1	163.7
18	24	1	211.6	219.8
21	24	1	170.9	172.0
4	25	1	75.1	67.3
7	25	1	21.6	18.1
10	25	1	59.2	58.6
13	25	1	42.6	41.3
16	25	1	49.9	51.4
19	25	1	44.1	37.0
2	26	1	14.8	21.8
5	26	1	271.5	270.5
8	26	1	151.1	162.3
11	26	1	84.2	78.5
14	26	1	48.6	43.6
17	26	1	9.1	8.2
20	26	1	17.9	18.6
23	26	1	24.5	26.2
0	27	1	54.6	54.2
3	27	1	67.4	72.9
6	27	1	100.5	93.1
9	27	1	39.0	42.2
15	27	1	84.3	84.6
18	27	1	44.6	42.4
21	27	1	20.5	24.1
24	27	1	6.3	3.5
1	28	1	12.7	3.1
7	28	1	93.5	90.3
13	28	1	95.2	90.1
16	28	1	77.4	82.7
19	28	1	19.6	20.2
22	28	1	34.4	32.8
2	29	1	179.5	173.7
5	29	1	101.9	100.4
8	29	1	70.5	76.5
11	29	1	106.0	97.7
14	29	1	93.5	86.6
17	29	1	52.0	53.9
20	29	1	170.2	158.2
23	29	1	93.4	79.9
26	29	1	83.3	85.6
1	30	1	21.6	17.2
4	30	1	92.5	86.0
10	30	1	23.8	24.4
13	30	1	12.8	20.5
1	31	1	92.0	83.7
4	31	1	23.1	27.9
7	31	1	84.2	73.5
10	31	1	128.2	126.4
H	K	L	F OBS	F CALC
-13	31	1	8.2	8.0
-11	15	1	61.8	59.2
-14	18	1	41.6	34.9
-14	21	1	125.3	119.6
-14	24	1	120.4	115.7
-14	30	1	33.9	29.0
-14	33	1	13.7	15.9
-15	17	1	151.3	138.7
-15	23	1	55.0	51.5
-15	26	1	41.6	39.2
-15	29	1	26.0	23.8
-15	32	1	7.6	15.6
-16	19	1	23.7	24.1
-16	22	1	36.9	30.8
-16	25	1	24.7	31.1
-16	28	1	26.8	24.1
-16	31	1	8.3	14.7
-17	18	1	12.6	13.0
-17	21	1	82.7	81.6
-17	24	1	9.8	13.6
-17	27	1	57.9	53.1
-18	20	1	60.8	47.5
-18	23	1	36.5	30.2
-18	26	1	25.8	29.7
-18	29	1	38.5	35.5
-19	22	1	47.6	35.7
-19	25	1	72.0	61.6
-19	28	1	53.5	43.4
-19	31	1	37.2	37.7
-20	21	1	65.0	67.8
-20	24	1	45.0	40.5
-20	27	1	50.2	49.3
-21	23	1	53.8	54.2
-21	26	1	57.5	58.2
-22	25	1	28.9	28.7
-22	28	1	15.6	13.3
-23	27	1	39.4	34.4
-24	24	1	9.2	3.5
5	0	2	98.8	95.8
8	0	2	173.3	178.9
11	0	2	68.1	63.7
17	0	2	55.1	59.2
20	0	2	41.2	42.5
26	0	2	16.0	14.6
29	0	2	35.2	41.5
3	1	2	312.5	321.1
6	1	2	284.9	297.3
9	1	2	11.1	18.1
12	1	2	133.4	122.2
15	1	2	61.2	58.9
18	1	2	7.8	10.0
21	1	2	47.5	43.0
24	1	2	27.4	30.7
27	1	2	14.2	11.1
1	2	2	225.6	231.6
4	2	2	260.4	265.1
7	2	2	50.3	47.0
10	2	2	77.9	88.6
13	2	2	17.6	15.0
16	2	2	39.2	34.9
22	2	2	9.0	5.2
25	2	2	39.2	36.2
28	2	2	19.3	22.8
2	3	2	27.3	32.1
5	3	2	143.4	137.4
8	3	2	9.8	16.3
11	3	2	41.9	36.0
14	3	2	124.4	117.2
17	3	2	85.3	81.3
23	3	2	17.3	17.3
26	3	2	29.7	32.2
0	4	2	321.7	318.1
3	4	2	101.2	97.5
6	4	2	18.9	21.4
9	4	2	6.3	4.2
12	4	2	25.4	30.1
15	4	2	27.2	33.7
18	4	2	20.2	23.5
21	4	2	23.8	20.9
24	4	2	33.5	32.8
1	5	2	39.1	31.7
4	5	2	42.9	41.5
7	5	2	25.4	20.6
13	5	2	51.3	45.9
16	5	2	129.1	128.3
19	5	2	27.2	31.1
22	5	2	22.6	19.6
2	6	2	14.8	21.8
5	6	2	271.5	270.5
8	6	2	151.1	162.3
11	6	2	84.2	78.5
14	6	2	48.6	43.6
17	6	2	9.1	8.2
20	6	2	17.9	18.6
23	6	2	24.5	26.2
0	7	2	54.6	54.2
3	7	2	67.4	72.9
6	7	2	100.5	93.1
9	7	2	39.0	42.2
15	7	2	84.3	84.6
18	7	2	44.6	42.4
21	7	2	20.5	24.1
24	7	2	6.3	3.5
1	8	2	12.7	3.1
7	8	2	93.5	90.3
13	8	2	95.2	90.1
16	8	2	77.4	82.7
19	8	2	19.6	20.2
22	8	2	34.4	32.8
2	9	2	179.5	173.7
5	9	2	101.9	100.4
8	9	2	70.5	76.5
11	9	2	106.0	97.7
14	9	2	93.5	86.6
17	9	2	52.0	53.9
20	9	2	170.2	158.2
23	9	2	93.4	79.9
26	9	2	83.3	85.6
1	10	2	21.6	17.2
4	10	2	92.5	86.0
10	10	2	23.8	24.4
13	10	2	12.8	20.5
1	11	2	92.0	83.7
4	11	2	23.1	27.9
7	11	2	84.2	73.5
10	11	2	128.2	126.4
H	K	L	F OBS	F CALC
13	11	2	27.3	24.5
16	11	2	34.6	28.7
19	11	2	27.3	28.8
2	12	2	9.0	3.1
5	12	2	18.6	22.4
11	12	2	71.2	67.4
14	12	2	25.7	30.7
23	12	2	10.6	1.2
0	13	2	3.8	6.8
3	13	2	18.2	12.7
6	13	2	24.2	27.9
12	13	2	41.9	40.1
18	13	2	16.7	17.8
21	13	2	12.5	11.4
1	14	2	44.1	37.0
4	14	2	26.6	28.5
10	14	2	41.7	35.1
13	14	2	41.1	38.5
2	15	2	100.7	94.4
5	15	2	41.8	34.6
8	15	2	60.5	68.8
11	15	2	20.3	20.3
17	15	2	19.6	18.2
20	15	2	19.4	19.0
0	16	2	15.8	6.2
6	16	2	75.8	69.4
9	16	2	28.9	24.4
12	16	2	23.1	24.4
15	16	2	22.8	25.2
4	17	2	28.0	23.4
7	17	2	82.2	69.7
13	17	2	8.0	6.5
16	17	2	19.7	20.5
1	18	2	35.0	38.1
4	18	2	22.1	26.1
7	18	2	9.7	6.2
0	19	2	79.1	64.9
3	19	2	35.2	34.4
6	19	2	22.3	22.1
9	19	2	36.4	31.5
12	19	2	20.9	22.9
1	20	2	30.4	25.2
4	20	2	9.1	7.2
7	20	2	15.2	6.4
10	20	2	35.6	35.7
13	20	2	16.0	17.4
16	20	2	41.8	38.5
5	21	2	16.4	11.6
8	21	2	47.5	43.0
11	21	2	6.6	9.2
14	21	2	35.4	25.4
17	21	2	46.2	47.6
20	21	2	28.6	25.9
1	22	2	27.4	30.7
4	22	2	20.5	16.1
7	22	2	39.1	37.2
10	22	2	14.7	12.4
13	22	2	29.7	29.6
16	22	2	29.2	27.0
2	23	2	30.6	24.1
5	23	2	16.4	17.6
8	23	2	17.3	21.2
11	23	2	41.9	36.6
14	23	2	35.6	25.4
17	23	2	20.2	29.4
0	24	2	17.9	13.9
3	24	2	10.1	19.1
6	24	2	10.7	7.3
12	24	2	284.0	288.0
15	24	2	167.1	163.7
18	24	2	211.6	219.8
21	24	2	170.9	172.0
4	25	2	75.1	67.3
7	25	2	21.6	18.1
10	25	2	59.2	58.6
13	25	2	42.6	41.3
16	25	2	49.9	51.4
19	25	2	44.1	37.0
2	26	2	14.8	21.8
5	26	2	271.5	270.5
8	26	2	151.1	162.3
11	26	2	84.2	78.5
14	26	2	48.6	43.6
17	26	2	9.1	8.2
20	26	2	17.9	18.6
23	26	2	24.5	26.2
0	27	2	54.6	54.2
3	27	2	67.4	72.9
6	27	2	100.5	93.1
9	27	2	39.0	42.2
15	27	2	84.3	84.6
18	27	2	44.6	42.4
21	27	2	20.5	24.1
24	27	2	6.3	3.5
1	28	2	12.7	3.1
7	28	2	93.5	90.3
13	28	2	95.2	90.1
16	28	2	77.4	82.7
19	28	2	19.6	20.2
22	28	2	34.4	32.8
2	29	2	179.5	173.7
5	29	2	101.9	100.4
8	29	2	70.5	76.5
11	29	2	106.0	97.7
14	29	2	93.5	86.6
17	29	2	52.0	53.9
20	29	2	170.2	158.2
23	29	2	93.4	79.9
26	29	2	83.3	85.6
1	30	2	21.6	17.2
4	30	2	92.5	86.0
10	30	2	23.8	24.4
13	30	2	12.8	20.5
1	31	2	92.0	83.7
4	31	2	23.1	27.9
7	31	2	84.2	73.5
10	31	2	128.2	126.4
-9	19	2	50.8	39.1
-9	25	2	38.7	32.9
-9	31	2	12.1	4.9
-10	12	2	109.6	109.1
-10	15	2	109.0	103.1
-10	18	2	48.4	39.6
-10	24	2	9.1	9.6
-10	27	2	33.4	31.2

H	K	L	F OBS	F CALC
10	6	3	52.7	44.0
21	6	3	40.0	39.8
24	6	3	16.1	10.3
1	7	3	135.7	127.5
4	7	3	115.7	114.2
5	7	3	47.1	47.8
10	7	3	66.6	64.6
13	7	3	31.5	34.1
16	7	3	30.3	22.1
19	7	3	61.1	53.0
22	7	3	24.5	22.4
2	8	3	145.3	145.9
5	8	3	135.3	147.2
8	8	3	45.5	43.2
11	8	3	116.3	117.9
14	8	3	63.3	66.7
17	8	3	8.8	13.3
20	8	3	8.0	5.7
23	8	3	10.9	15.4
0	9	3	31.8	28.1
3	9	3	11.9	6.2
7	9	3	146.5	143.0
12	9	3	22.2	16.4
18	9	3	23.8	14.7
4	10	3	206.6	200.9
7	10	3	97.2	95.4
10	10	3	11.5	14.9
13	10	3	29.5	34.7
19	10	3	19.0	16.8
8	11	3	38.8	36.9
11	11	3	134.5	133.9
13	11	3	37.7	33.4
20	11	3	24.3	22.9
0	12	3	38.2	35.9
3	12	3	24.6	27.3
6	12	3	56.7	45.0
9	12	3	63.8	62.3
12	12	3	23.2	19.9
15	12	3	24.1	24.2
18	12	3	7.4	9.4
21	12	3	10.7	13.0
1	13	3	6.9	1.9
4	13	3	106.6	105.5
7	13	3	37.7	39.6
13	13	3	56.4	48.8
19	13	3	10.9	15.7
2	14	3	14.9	10.4
5	14	3	8.1	3.3
14	14	3	21.8	18.7
17	14	3	9.9	6.5
20	14	3	9.1	10.5
0	15	3	73.8	86.2
6	15	3	60.1	54.3
9	15	3	37.3	29.3
12	15	3	12.1	2.3
18	15	3	9.8	6.2
4	16	3	38.6	37.5
7	16	3	24.8	17.2
10	16	3	19.4	14.1
16	16	3	6.4	10.3
2	17	3	32.4	34.4
5	17	3	58.4	63.0
8	17	3	24.2	18.5
11	17	3	37.7	34.4
17	17	3	29.6	30.6
0	18	3	31.2	27.2
3	18	3	22.9	23.5
6	18	3	45.6	36.6
9	18	3	11.9	15.5
12	18	3	25.7	27.8
1	19	3	17.3	18.3
4	19	3	29.1	27.3
7	19	3	57.4	43.2
10	19	3	11.0	8.5
11	20	3	17.9	19.5
3	21	3	15.0	16.5
6	21	3	29.2	24.0
9	21	3	7.1	11.9
12	21	3	22.6	24.6
1	22	3	56.4	46.8
4	22	3	14.4	18.1
10	22	3	15.5	16.4
2	23	3	50.1	42.3
5	23	3	45.5	40.3
8	23	3	16.6	15.4
11	23	3	41.0	37.2
3	24	3	32.7	24.9
6	24	3	9.3	6.8
4	25	3	6.7	1.4
7	25	3	18.2	20.7
5	26	3	16.3	3.5
0	27	3	19.5	21.6
1	28	3	8.1	6.9
-1	2	3	59.3	57.1
-1	5	3	19.8	21.9
-1	11	3	11.7	1.6
-1	14	3	79.7	78.7
-1	17	3	22.4	21.3
-1	20	3	39.6	32.1
-1	23	3	26.1	26.7
-1	29	3	5.7	8.5
-2	4	3	162.8	159.3
-2	7	3	172.1	175.2
-2	10	3	101.6	113.1
-2	16	3	19.7	21.4
-2	22	3	30.4	26.2
-3	6	3	115.6	98.1
-3	9	3	115.6	116.5
-3	12	3	103.6	105.7
-3	18	3	43.7	38.2
-3	21	3	21.2	24.4
-3	30	3	35.3	28.7
-4	3	3	109.9	112.6
-4	8	3	115.5	106.9
-4	11	3	87.4	82.9
-4	14	3	76.0	76.8
-4	17	3	7.6	11.0
-4	20	3	11.9	10.9
-4	23	3	29.1	27.2
-4	26	3	65.8	60.4
-4	29	3	6.7	13.4
-5	1	3	90.4	86.2
-5	10	3	38.4	40.1
-5	13	3	188.4	182.8
-5	19	3	44.6	40.6
-5	22	3	46.4	47.0
-5	25	3	31.2	29.4
-5	28	3	26.2	22.1
-5	31	3	12.2	12.7
-6	9	3	91.0	97.6
-6	12	3	103.2	101.3
-6	15	3	30.9	35.7
-6	18	3	32.7	22.1
-6	21	3	31.4	32.7
-6	24	3	36.9	48.4
-6	27	3	25.9	23.3
-6	30	3	11.4	14.1
-7	8	3	79.5	78.0
-7	11	3	107.4	100.2
-7	14	3	50.9	50.4
-7	17	3	66.2	60.1
-7	20	3	47.2	36.0
-7	23	3	21.4	13.4
-7	26	3	24.2	13.0
-7	32	3	7.2	10.3
-8	10	3	78.7	89.6
-8	13	3	187.0	180.8
-8	16	3	59.2	60.6
-8	19	3	27.4	29.2
-8	22	3	36.5	33.1
-8	25	3	54.6	45.3
-8	28	3	21.2	25.1
-8	31	3	15.4	16.3
-9	12	3	47.2	54.2
-9	15	3	81.0	79.0
-9	18	3	112.0	105.0
-9	24	3	15.2	15.5
-9	27	3	61.9	60.7
-9	30	3	12.3	16.3
-10	11	3	67.9	63.6
-10	14	3	102.0	100.7
-10	20	3	27.6	34.0
-10	23	3	82.6	64.9
-10	29	3	26.9	27.1
-11	13	3	43.0	46.9
-11	16	3	80.1	88.6
-11	19	3	62.8	50.2
-11	22	3	57.5	55.9
-11	25	3	21.5	20.9
-11	28	3	11.6	14.4
-11	31	3	28.6	28.2
-12	18	3	56.7	45.2
-12	24	3	17.6	15.9
-12	27	3	21.2	21.1
-12	30	3	21.0	23.9
-13	13	3	10.7	9.4
-13	16	3	95.0	91.7
-13	17	3	75.2	62.4
-13	20	3	55.3	60.1
-13	26	3	69.1	61.7
-13	32	3	12.5	17.9
-14	16	3	18.3	20.0
-14	19	3	28.0	31.3
-14	22	3	66.3	70.0
-14	25	3	20.2	18.7
-14	28	3	18.5	19.2
-14	31	3	7.0	2.9
-15	15	3	58.4	54.4
-15	21	3	12.0	7.4
-15	24	3	38.9	35.5
-15	27	3	25.6	26.1
-15	30	3	13.6	11.3
-16	33	3	14.9	11.6
-16	20	3	66.8	60.8
-16	23	3	42.9	43.8
-16	26	3	39.8	30.8
-16	29	3	7.9	10.7
-17	19	3	144.7	146.5
-17	22	3	101.2	102.0
-17	31	3	66.2	57.5
-18	21	3	70.2	67.5
-18	24	3	32.6	32.7
-18	33	3	18.7	17.6
-19	20	3	22.9	14.7
-19	29	3	25.7	20.4
-19	32	3	9.3	7.4
-20	25	3	30.1	29.0
-20	28	3	13.9	14.6
-20	31	3	9.5	7.4
-21	30	3	30.2	28.5
-21	33	3	31.2	27.5
-23	26	3	21.4	23.9
-24	27	3	26.7	22.4
-1	0	4	40.9	33.2
-1	3	4	75.4	75.8
-1	7	4	152.1	144.3
-1	10	4	89.0	83.0
-1	13	4	58.3	44.0
-1	16	4	92.7	44.1
-1	19	4	89.0	84.2
-1	25	4	68.8	67.1
-1	28	4	14.8	16.6
-1	31	4	14.9	17.0
-2	0	4	14.3	4.2
-2	5	4	8.3	17.4
-2	8	4	150.4	158.9
-2	11	4	47.4	65.6
-2	14	4	23.3	24.5
-2	17	4	30.2	37.4
-2	20	4	32.0	24.8
-2	23	4	55.9	55.6
-2	26	4	46.0	45.3
-2	29	4	11.6	12.7
-3	2	4	84.5	82.1
-3	6	4	71.6	73.9
-3	9	4	48.4	49.3
-3	12	4	13.5	13.1
-3	15	4	119.6	129.4
-3	18	4	20.1	17.0
-3	21	4	33.7	38.0
-3	24	4	71.6	75.1
-3	27	4	19.4	14.2
-3	30	4	21.9	20.2
-4	1	4	6.9	11.9
-4	4	4	158.1	152.0
-4	7	4	34.5	23.7
-4	13	4	20.1	17.0
-4	16	4	33.7	38.0
-4	19	4	71.6	75.1
-4	22	4	19.4	14.2
-4	25	4	21.9	20.2
-4	28	4	6.9	11.9
-5	5	4	158.1	152.0
-5	9	4	15.2	13.1
-5	15	4	51.1	43.7
-5	18	4	19.3	17.1
-5	21	4	49.1	47.4
-5	30	4	22.3	23.8
-6	8	4	32.1	33.3
-6	11	4	209.8	207.4
-6	14	4	83.8	87.8
-6	17	4	19.4	19.1
-6	20	4	74.9	67.0
-6	23	4	63.7	65.8
-6	26	4	16.4	19.2
-7	10	4	33.1	33.8
-7	13	4	14.0	9.2
-7	16	4	93.7	87.8
-7	19	4	13.9	19.4
-7	22	4	33.3	31.0
-7	25	4	19.0	21.0
-8	9	4	61.3	61.4
-8	12	4	3.2	5.7
-8	15	4	71.5	66.3
-8	18	4	98.6	95.9
-8	21	4	39.6	39.9
-8	24	4	21.2	21.4
-8	27	4	22.7	24.8
-8	30	4	15.9	19.8
-9	11	4	109.8	116.2
-9	14	4	48.7	54.9
-9	17	4	95.0	89.5
-9	20	4	60.4	54.4
-9	23	4	73.4	77.6
-9	29	4	49.6	50.2
-10	13	4	35.3	34.1
-10	16	4	65.0	59.2
-10	19	4	39.2	35.5
-10	22	4	28.4	20.1
-10	25	4	21.0	14.4
-10	28	4	13.5	7.9
-10	31	4	13.7	10.5
-11	12	4	21.1	30.1
-11	15	4	14.4	19.7
-11	18	4	43.3	48.0
-11	21	4	66.8	57.1
-11	24	4	33.5	32.0
-11	27	4	31.8	32.5
-11	30	4	16.3	17.5
-12	14	4	18.3	9.2
-12	17	4	60.3	55.7
-12	20	4	40.4	44.5
-12	23	4	9.7	7.5
-13	16	4	74.3	71.3
-13	19	4	103.0	106.0
-13	25	4	63.2	60.4
-13	28	4	28.6	31.4
-13	31	4	25.0	24.2
-14	15	4	7.4	9.3
-14	18	4	43.6	35.6
-14	21	4	68.0	71.7
-14	24	4	30.0	33.2
-14	27	4	31.9	30.4
-14	33	4	13.0	11.4
-15	17	4	139.1	146.7
-15	23	4	50.3	47.6
-15	26	4	50.6	59.3
-15	26	4	31.6	29.3
-15	29	4	28.3	24.1
-16	25	4	30.9	24.6
-16	28	4	29.7	30.5
-16	31	4	27.7	28.7
-17	18	4	74.4	72.1
-17	21	4	24.3	31.2
-17	24	4	21.1	20.3
-17	27	4	19.9	17.9
-18	20	4	29.6	24.7
-18	23	4	17.3	16.0
-18	26	4	15.4	39.6
-18	29	4	7.1	9.4
-19	22	4	27.4	21.7
-19	25	4	45.6	43.8
-19	28	4	18.9	19.3
-19	31	4	24.7	25.7
-20	21	4	68.8	67.1
-20	24	4	20.9	19.0
-20	30	4	18.0	22.3
-20	33	4	20.4	21.0
-21	26	4	28.0	29.5
-21	25	4	40.0	34.3
-23	24	4	18.4	15.7
-23	30	4	21.9	25.5
-24	27	4	31.2	27.9
-24	30	4	21.6	21.0
-24	32	4	23.2	9.1
-25	28	4	36.6	32.0
-1	3	5	110.6	105.9
-1	6	5	19.7	4.3
-1	9	5	124.9	140.6
-1	12	5	19.7	22.2
-1	15	5	65.6	64.1
-1	18	5	22.7	19.4
-1	21	5	65.6	57.5
-1	24	5	46.0	45.3
-1	27	5	39.6	32.1
-2	5	5	15.8	14.8
-2	8	5	14.3	4.2
-2	11	5	8.3	17.4
-2	14	5	150.4	158.9
-2	17	5	47.4	65.6
-2	20	5	30.2	37.4
-2	23	5	32.0	24.8
-2	26	5	55.9	55.6
-3	7	5	46.0	45.3
-3	10	5	11.6	12.7
-3	13	5	84.5	82.1
-3	16	5	71.6	73.9
-3	19	5	48.4	49.3
-3	22	5	13.5	13.1
-3	25	5	34.5	23.7
-4	2	5	20.1	17.0
-4	5	5	33.7	38.0
-4	8	5	71.6	75.1
-4	11	5	19.4	14.2
-4	14	5	21.9	20.2
-4	17	5	6.9	11.9
-5	6	5	158.1	152.0
-5	9	5	15.2	13.1
-5	15	5	51.1	43.7
-5	18	5	19.3	17.1
-5	21	5	49.1	47.4
-5	30	5	22.3	23.8
-6	8	5	32.1	33.3
-6	11	5	209.8	207.4
-6	14	5	83.8	87.8
-6	17	5	19.4	19.1
-6	20	5	74.9	67.0
-6	23	5	63.7	65.8
-6	26	5	16.4	19.2
-7	10	5	33.1	33.8
-7	13	5	14.0	9.2
-7	16	5	93.7	87.8
-7	19	5	13.9	19.4
-7	22	5	33.3	31.0
-7	25	5	19.0	21.0
-8	9	5	61.3	61.4
-8	12	5	3.2	5.7
-8	15	5	71.5	66.3
-8	18	5	98.6	95.9
-8	21	5	39.6	39.9
-8	24	5	21.2	21.4
-8	27	5	22.7	24.8
-8	30	5	15.9	19.8
-9	11	5	109.8	116.2
-9	14	5	48.7	54.9
-9	17	5	95.0	89.5
-9	20	5	60.4	54.4
-9	23	5	73.4	77.6
-9	29	5	49.6	50.2
-10	13	5	35.3	34.1
-10	16	5	65.0	59.2
-10	19	5	39.2	35.5
-10	22	5	28.4	20.1
-10	25	5	21.0	14.4
-10	28	5	13.5	7.9
-10	31	5	13.7	10.5
-11	12	5	21.1	30.1
-11	15	5	14.4	19.7
-11	18	5	43.3	48.0
-11	21	5	66.8	57.1
-11	24	5	33.5	32.0
-11	27	5	31.8	32.5
-11	30	5	16.3	17.5
-12	14	5	18.3	9.2
-12	17	5	60.3	55.7
-12	20	5	40.4	44.5
-12	23	5	9.7	7.5
-13	16	5	74.3	71.3
-13	19	5	103.0	106.0
-13	25	5	63.2	60.4
-13	28	5	28.6	31.4
-13	31	5	25.0	24.2
-14	15	5	7.4	9.3
-14	18	5	43.6	35.6
-14	21	5	68.0	71.7
-14	24	5	30.0	33.2
-14	27	5	31.9	30.4
-14	33	5	13.0	11.4
-15	17	5	139.1	146.7
-15	23	5	50.3	47.6
-15	26	5	50.6	59.3
-15	26	5	31.6	29.3
-15	29	5	28.3	24.1
-16	25	5	30.9	24.6
-16	28	5	29.7	30.5
-16	31	5	27.7	28.7
-17	18	5	74.4	72.1
-17	21	5	24.3	31.2
-17	24	5	21.1	20.3
-17	27	5	19.9	17.9
-18	20	5	29.6	24.7
-18	23	5	17.3	16.0
-18	26	5	15.4	39.6
-18	29	5	7.1	9.4
-19	22	5	27.4	21.7
-19	25	5	45.6	43.8
-19	28	5	18.9	19.3
-19	31	5	24.7	25.7
-20	21	5	68.8	67.1
-20	24	5	20.9	19.0
-20	30	5	18.0	22.3
-20	33	5	20.4	21.0
-21	26	5	28.0	29.5
-23	25	5	40.0	34.3
-23	24	5	18.4	15.7
-23	30	5	21.9	25.5
-24	27	5	31.2	27.9
-24	30	5	21.6	21.0
-24	32	5	23.2	9.1
-25	28	5	36.6	32.0
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-1	6	6	19.7	4.3
-1	9	6	124.9	140.6
-1	12	6	19.7	22.2
-1	15	6	65.6	64.1
-1	18	6	22.7	19.4
-1	21	6	65.6	57.5
-1	24	6	46.0	45.3
-1	27	6	39.6	32.1
-2	5	6	15.8	14.8
-2	8	6	14.3	4.2
-2	11	6	8.3	17.4
-2	14	6	150.4	158.9
-2	17	6	47.4	65.6
-2	20	6	30.2	37.4
-2	23	6	32.0	24.8
-2	26	6	55.9	55.6
-3	7	6	46.0	45.3
-3	10	6	11.6	12.7
-3	13	6	84.5	82.1
-3	16	6	71.6	73.9
-3	19	6	48.4	49.3
-3	22	6	13.5	13.1
-3	25	6	34.5	23.7
-4	2	6	20.1	17.0
-4	5	6	33.7	38.0
-4	8	6	71.6	75.1
-4	11	6	19.4	14.2
-4	14	6	21.9	20.2
-4	17	6	6.9	11.9
-5	6	6	158.1	152.0
-5	9	6	15.2	13.1
-5	15	6	51.1	43.7
-5	18	6	19.3	17.1
-5	21	6	49.1	47.4
-5	30	6	22.3	23.8
-6	8	6	32.1	33.3
-6	11	6	209.8	207.4
-6	14	6	83.8	87.8
-6	17	6	19.4	19.1
-6	20	6	74.9	67.0
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-6	26	6	16.4	19.2
-7	10	6	33.1	33.8
-7	13	6	14.0	9.2
-7	16	6	93.7	87.8
-7	19	6	13.9	19.4
-7	22	6	33.3	31.0
-7	25	6	19.0	21.0
-8	9	6	61.3	61.4
-8	12	6	3.2	5.7
-8	15	6	71.5	66.3
-8	18	6	98.6	95.9
-8	21	6	39.6	39.9
-8	24	6	21.2	21.4
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-8	30	6	15.9	19.8
-9	11	6	109.8	116.2
-9	14	6	48.7	54.9
-9	17	6	95.0	89.5
-9	20	6	60.4	54.4
-9	23	6	73.4	77.6
-9	29	6	49.6	50.2
-10	13	6	35.3	34.1
-10	16	6	65.0	59.2
-10	19	6	39.2	35.5
-10	22	6	28.4	20.1
-10	25	6	21.0	14.4
-10	28	6	13.5	7.9
-10	31	6	13.7	10.5
-11	12	6	21.1	30.1
-11	15	6	14.4	19.7
-11	18	6	43.3	48.0
-11	21	6	66.8	57.1
-11	24	6	33.5	32.0
-11	27	6	31.8	32.5
-11	30	6	16.3	17.5
-12	14	6	18.3	9.2
-12	17	6	60.3	55.7
-12	20	6	40.4	44.5
-12	23	6	9.7	7.5
-13	16	6	74.3	71.3
-13	19	6	103.0	106.0
-13	25	6	63.2	60.4
-13	28	6	28.6	31.4
-13	31	6	25.0	24.2
-14	15	6	7.4	9.3
-14	18	6	43.6	35.6
-14	21	6	68.0	71.7
-14	24	6	30.0	33.2
-14	27	6	31.9	30.4
-14	33	6	13.0	11.4
-15	17	6	139.1	146.7
-15	23	6	50.3	47.6
-15	26	6	50.6	59.3
-15	26	6	31.6	29.3
-15	29	6	28.3	24.1
-16	25	6	30.9	24.6
-16	28	6	29.7	30.5
-16	31	6	27.7	28.7
-17	18	6	74.4	72.1
-17	21	6	24.3	31.2
-17	24	6	21.1	20.3
-17	27	6	19.9	17.9
-18	20	6	29.6	24.7
-18	23	6	17.3	16.0
-18	26	6	15.4	39.6
-18	29	6	7.1	9.4
-19	22	6	27.4	21.7
-19	25	6	45.6	43.8
-19	28	6	18.9	19.3
-19	31	6	24.7	25.7
-20	21	6	68.8	67.1
-20	24	6	20.9	19.0
-20	30	6	18.0	22.3
-20	33	6	20.4	21.0
-21	26	6	28.0	29.5
-23	25	6	40.0	34.3
-23	24	6	18.4	15.7
-23	30	6	21.9	25.5
-24	27	6	31.2	27.9
-24	30	6	21.6	21.0
-24	32	6	23.2	9.1
-25	28	6	36.6	32.0
-1	3	7	110.6	105.9
-1	6	7	19.7	4.3
-1	9	7	124.9	140.6
-1	12	7	19.7	22.2
-1	15	7	65.6	64.1
-1	18	7	22.7	19.4
-1	21	7	65.6	57.5
-1	24	7	46.0	45.3
-1	27	7	39.6	32.1
-2	5	7	15.8	14.8
-2	8	7	14.3	4.2
-2	11	7	8.3	17.4
-2	14	7	150.4	158.9
-2	17	7	47.4	65.6
-2	20	7	30.2	37.4
-2	23	7	32.0	24.8
-2	26	7	55.9	55.6
-3	7	7	46.0	45.3
-3	10	7	11.6	12.7
-3	13	7	84.5

H	K	L	F OBS	F CALC
4	7	6	8.7	4.5
7	7	6	66.4	54.7
16	7	6	27.2	19.2
19	7	6	7.3	9.2
2	8	6	43.8	50.0
5	8	6	92.7	99.9
8	8	6	27.2	25.2
11	8	6	46.8	47.5
14	8	6	18.6	16.0
17	8	6	38.2	40.1
0	9	6	111.9	113.1
3	9	6	6.6	14.6
9	9	6	39.1	45.3
12	9	6	28.9	28.3
18	9	6	10.0	9.9
1	10	6	64.2	71.4
4	10	6	27.6	24.3
7	10	6	7.8	8.8
10	10	6	21.9	21.7
13	10	6	55.5	57.4
16	10	6	15.2	13.6
19	10	6	29.7	37.5
11	11	6	8.3	7.4
14	11	6	30.7	35.6
17	11	6	6.6	3.0
0	12	6	51.1	40.2
6	12	6	105.2	101.6
9	12	6	45.6	47.8
12	12	6	8.1	2.9
15	12	6	17.6	18.7
18	12	6	23.8	19.5
1	13	6	24.7	19.1
4	13	6	26.3	27.6
7	13	6	51.7	40.2
2	14	6	62.4	59.1
14	14	6	46.1	38.8
0	15	6	19.2	14.3
3	15	6	21.6	19.4
6	15	6	23.6	20.5
9	15	6	8.1	10.9
12	15	6	35.7	28.3
4	16	6	16.7	1.3
7	16	6	34.8	31.8
8	17	6	38.2	35.5
0	18	6	22.0	28.3
3	18	6	45.5	39.6
6	18	6	27.5	30.3
9	18	6	56.3	56.0
1	19	6	43.2	41.4
7	19	6	40.2	39.1
2	20	6	39.6	36.6
5	20	6	16.8	15.1
8	20	6	25.0	24.2
0	21	6	22.9	25.0
3	21	6	32.2	37.7
6	21	6	18.9	15.7
9	21	6	13.7	15.9
1	22	6	32.5	32.1
4	22	6	37.6	30.7
7	22	6	9.3	14.1
5	23	6	24.6	30.7
0	24	6	7.0	5.1
3	24	6	34.5	29.6
1	25	6	27.0	26.3
-1	2	6	24.7	22.1
-1	5	6	32.4	37.1
-1	8	6	22.0	19.7
-1	11	6	18.3	15.3
-1	14	6	113.9	114.5
-1	17	6	101.8	90.4
-1	20	6	22.0	17.2
-1	23	6	7.7	8.8
-2	4	6	41.0	29.4
-2	7	6	28.9	30.0
-2	10	6	28.9	21.2
-2	13	6	28.7	26.2
-2	16	6	115.6	127.9
-2	19	6	37.9	39.5
-2	22	6	11.4	6.3
-2	25	6	13.9	10.3
-3	6	6	87.7	82.9
-3	9	6	109.7	108.8
-3	12	6	21.7	16.0
-3	15	6	77.5	76.1
-3	18	6	64.9	60.6
-3	21	6	45.5	35.5
-3	24	6	7.5	8.1
-4	5	6	15.8	14.3
-4	8	6	102.4	111.9
-4	14	6	150.5	151.3
-4	20	6	22.0	17.6
-4	23	6	18.0	18.8
-4	26	6	37.6	34.2
-5	7	6	96.8	99.6
-5	10	6	17.3	14.6
-5	13	6	24.3	20.8
-5	16	6	126.4	120.9
-5	22	6	27.4	22.3
-5	25	6	13.0	4.5
-6	9	6	121.0	121.2
-6	12	6	24.8	26.4
-6	15	6	94.8	98.8
-6	18	6	25.4	19.8
-6	21	6	18.6	19.2
-6	24	6	28.6	25.3
-6	27	6	22.2	13.1
-7	8	6	12.6	11.0
-7	11	6	15.0	15.0
-7	17	6	160.4	152.7
-7	20	6	24.9	18.4
-7	26	6	14.7	14.3
-8	10	6	75.8	84.5
-8	13	6	42.1	46.4
-8	16	6	23.8	19.0
-8	19	6	119.8	108.7
-8	22	6	47.8	42.2
-8	25	6	35.7	33.1
-9	12	6	13.1	14.9
-9	15	6	53.9	54.7
-9	18	6	60.6	57.1
-9	21	6	54.0	45.5
-9	24	6	22.9	16.1
-9	27	6	42.6	43.2
-10	11	6	6.5	8.6
-10	17	6	13.5	17.0
-10	20	6	11.7	13.4
-10	23	6	49.6	46.9

H	K	L	F OBS	F CALC
-10	26	6	50.9	46.5
-11	16	6	31.4	27.6
-11	19	6	31.2	26.6
-11	25	6	27.4	24.5
-12	18	6	44.0	45.2
-12	21	6	66.1	57.6
-12	24	6	54.6	60.5
-12	27	6	41.8	40.3
-13	14	6	67.0	78.0
-13	17	6	45.6	41.1
-13	20	6	70.3	62.1
-13	23	6	8.3	9.5
-13	26	6	18.8	19.3
-13	29	6	11.0	11.0
-14	16	6	20.8	15.5
-14	19	6	96.9	100.5
-14	25	6	25.6	29.8
-14	28	6	6.9	8.3
-15	18	6	47.1	53.1
-15	24	6	30.3	27.6
-16	26	6	27.3	26.4
-17	22	6	8.3	10.0
-20	22	6	19.8	32.8
-20	25	6	16.8	22.5
-21	24	6	10.8	11.7
-22	23	6	60.8	67.0
-23	25	6	27.0	26.7
1	0	7	21.3	26.3
4	0	7	22.2	26.5
7	0	7	48.3	41.7
10	0	7	58.5	55.6
13	0	7	26.6	21.3
19	0	7	28.6	27.0
22	0	7	13.3	3.6
25	0	7	2.9	25.5
2	1	7	29.8	36.0
5	1	7	37.2	50.9
8	1	7	40.5	36.8
11	1	7	29.7	21.3
14	1	7	48.2	54.4
17	1	7	31.7	26.3
20	1	7	7.1	5.8
23	1	7	23.2	20.1
26	1	7	8.8	11.8
0	2	7	124.4	135.1
3	2	7	49.2	51.3
6	2	7	16.7	22.7
12	2	7	13.5	12.0
15	2	7	71.6	80.3
18	2	7	49.5	39.9
24	2	7	33.8	32.2
1	3	7	21.9	22.7
4	3	7	101.3	110.3
7	3	7	71.7	89.1
10	3	7	65.1	56.8
13	3	7	65.0	70.3
16	3	7	7.5	8.1
22	3	7	43.5	46.3
2	4	7	44.4	47.9
5	4	7	26.4	27.1
8	4	7	13.6	22.5
11	4	7	44.6	49.2
14	4	7	8.7	16.0
17	4	7	18.0	16.2
23	4	7	13.1	8.4
0	5	7	17.0	17.7
3	5	7	30.5	42.7
6	5	7	62.5	70.1
9	5	7	60.8	64.4
12	5	7	10.6	15.9
15	5	7	7.0	8.8
21	5	7	24.5	23.2
0	6	7	21.9	25.8
4	6	7	15.8	4.7
7	6	7	47.0	40.6
10	6	7	44.3	44.3
13	6	7	42.8	38.2
16	6	7	25.2	18.4
19	6	7	12.8	13.1
22	6	7	44.3	42.9
25	6	7	92.9	100.7
1	7	7	41.2	42.3
4	7	7	41.2	41.2
7	7	7	22.0	31.9
10	7	7	17.6	16.5
13	7	7	107.2	105.9
16	7	7	84.6	83.9
19	7	7	57.3	51.1
22	7	7	29.0	25.3
25	7	7	30.4	32.2
28	7	7	18.2	20.9
1	8	7	18.5	23.0
4	8	7	51.4	54.4
7	8	7	40.6	35.4
10	8	7	22.2	16.9
19	8	7	22.3	22.2
2	10	7	28.4	21.5
5	10	7	50.8	38.7
8	10	7	12.7	14.0
11	10	7	5.9	7.1
0	11	7	132.0	146.2
3	11	7	24.5	18.0
9	11	7	57.4	48.3
12	11	7	17.7	17.3
15	11	7	74.5	61.7
18	11	7	15.2	14.4
21	11	7	43.9	45.7
24	11	7	54.4	53.1
27	11	7	36.3	25.1
30	11	7	38.7	31.4
1	12	7	34.1	36.5
4	12	7	44.4	44.2
7	12	7	47.1	49.7
10	12	7	50.8	38.7
13	12	7	37.4	35.6
16	12	7	20.7	21.7

H	K	L	F OBS	F CALC
15	1	8	47.6	42.5
18	1	8	21.8	19.7
21	1	8	25.6	24.5
24	1	8	47.2	45.0
1	2	8	117.9	123.2
4	2	8	20.3	18.0
7	2	8	15.1	14.7
10	2	8	22.2	20.6
13	2	8	41.9	37.8
16	2	8	40.7	35.5
22	2	8	9.1	10.6
2	3	8	43.6	45.7
5	3	8	8.9	5.7
8	3	8	77.2	64.4
14	3	8	30.2	21.7
23	3	8	15.8	17.3
0	4	8	20.7	13.4
3	4	8	65.5	73.9
6	4	8	29.7	31.5
9	4	8	29.8	20.3
12	4	8	51.6	50.2
15	4	8	27.3	31.4
18	4	8	28.0	29.7
1	5	8	41.0	53.0
4	5	8	66.0	70.7
7	5	8	59.1	67.2
10	5	8	13.7	12.5
13	5	8	58.5	45.9
16	5	8	50.1	45.6
19	5	8	35.1	38.1
22	5	8	17.5	16.3
2	6	8	22.0	14.5
5	6	8	29.3	25.1
8	6	8	39.9	37.7
11	6	8	36.1	35.1
14	6	8	17.2	10.1
17	6	8	16.8	12.5
20	6	8	8.6	7.8
0	7	8	75.2	77.5
3	7	8	38.7	34.3
6	7	8	1.6	1.6
9	7	8	7.0	3.3
15	7	8	32.9	35.3
21	7	8	11.0	12.4
24	7	8	17.0	11.0
4	8	8	14.0	14.0
7	8	8	8.2	10.4
19	8	8	17.9	16.5
2	9	8	10.7	12.2
8	9	8	17.7	9.4
8	9	8	23.4	22.3
11	9	8	32.3	27.3
14	9	8	6.5	12.0
17	9	8	22.2	14.7
0	10	8	4.1	5.2
3	10	8	37.2	32.1
6	10	8	26.1	25.7
15	10	8	32.4	32.8
18	10	8	13.8	10.9
1	11	8	43.7	44.3
10	11	8	34.1	32.7
13	11	8	24.4	21.2
16	11	8	15.0	11.0
2	12	8	54.3	55.7
11	12	8	36.1	28.6
14	12	8	9.1	3.2
17	12	8	16.3	20.5
0	13	8	90.5	99.3
3	13	8	42.3	40.7
6	13	8	20.1	15.5
12	13	8	11.8	13.6
15	13	8	24.3	19.2
1	14	8	25.4	16.6
4	14	8	40.8	32.6
13	14	8	5.1	6.4
2	15	8	58.4	55.9
5	15	8	32.0	27.7
11	15	8	18.3	14.4
0	16	8	18.8	17.5
6	16	8	30.5	28.1
9	16	8	21.7	20.9
12	16	8	15.2	13.3
1	17	8	15.7	10.4
4	17	8	38.2	38.6
7	17	8	6.1	8.5
2	18	8	10.0	7.6
5	18	8	16.5	14.6
8	18	8	23.1	23.8
3	19	8	50.4	41.1
6	19	8	5.5	6.0
1	20	8	18.2	18.5
4	20	8	9.9	10.5
7	20	8	29.7	27.6
0	22	8	39.0	40.4
3	22	8	32.9	28.5
1	23	8	5.0	6.1
4	23	8	36.3	45.7
-1	6	8	41.0	43.7
-1	9	8	17.9	24.0
-1	15	8	40.4	36.6
-1	18	8	10.0	11.3
-1	21	8	11.1	9.5
-2	8	8	15.6	11.6
-2	11	8	90.4	105.7
-2	14	8	45.9	44.3
-2	23	8	23.9	24.6
-3	4	8	13.0	12.0
-3	10	8	116.1	132.9
-3	16	8	63.5	75.4
-3	19	8	45.5	44.1
-3	22	8	11.0	10.4
-3	25	8	38.9	32.1
-4	6	8	44.1	54.3
-4	9	8	29.9	25.0
-4	12	8	17.7	15.5
-4	15	8	56.5	51.5
-4	18	8	47.7	56.0
-4	21	8	30.9	23.2
-4	24	8	49.2	35.1
-5	8	8	50.9	47.4
-5	11	8	35.7	29.8

H	K	L	F OBS	F CALC
13	4	8	13.4	6.1
16	4	8	30.0	25.2
19	4	8	55.4	55.1
5	5	8	15.3	13.7
8	5	8	4.7	1.9
11	5	8	56.8	53.6
17	5	8	27.4	27.2
20	5	8	36.2	37.3
23	5	8	20.1	15.0
0	6	8	14.9	14.0
6	6	8	15.6	10.1
9	6	8	20.7	15.5
12	6	8	32.6	23.0
15	6	8	31.7	35.3
18	6	8	35.1	43.0
21	6	8	44.6	49.6
24	6	8	76.3	81.9
27	6	8	15.9	19.8
3	7	8	21.7	20.6
9	7	8	32.7	32.0
12	7	8	31.9	26.6
15	7	8	13.1	16.4
18	7	8	40.7	39.2
21	7	8	55.5	57.3
-10	12	8	22.2	17.4
-10	15	8	18.1	13.6
-10	18	8	38.9	42.9
-10	24	8	17.8	19.6
-10	27	8	16.3	13.4
-11	14	8	86.2	96.0
-11	17	8	15.8	1.1
-12	13	8	33.0	24.1
-12	16	8	32.2	25.0
-12	19	8	47.6	49.7
-12	25	8	18.9	18.1
-12	28	8	26.2	33.6
-13	15	8	38.3	39.6
-13	21	8	36.0	36.2
-13	24	8	6.3	7.6
-13	27	8	16.0	14.0
-14	17	8	36.9	32.5
-14	20	8	18.6	13.4
-14	23	8	46.1	47.6
-14	26	8	40.8	33.4
-15	19	8	30.1	31.4
-15	19	8	36.7	30.3
-15	22	8	32.9	26.1
-15	28	8	26.6	27.2
-16	18	8	18.7	18.0
-16	21	8	31.2	26.0
-16	24	8	49.0	47.0
-17	26	8	42.7	34.4
-18	19	8	24.9	28.1
-18	22	8	8.4	13.4
-18	25	8	18.5	17.5
-19	23	8	19.3	17.6
-22	24	8	9.1	1.5
-24	25	8	25.2	25.2
3	0	9	12.3	14.1
6	0	9	62.7	72.3
9	0	9	14.7	9.9
12	0	9	26.7	19.2
18	0	9	35.6	36.0
21	0	9	16.0	14.6
1	1	9	14.7	14.5
7	1	9	52.4	63.7
10	1	9	12.0	11.5
13	1	9	60.7	68.7
16	1	9	50.3	48.4
19	1	9	34.5	25.6
22	1	9	12.1	8.5
25	1	9	25.9	30.5
2	2	9	10.3	10.1
5	2	9	10.2	7.2
8	2	9	17.6	12.3
11	2	9	25.3	23.7
14	2	9	58.8	57.5
17	2	9	6.6	1.2
20	2	9	53.3	64.7
23	2	9	72.0	75.1
26	2	9	11.0	6.6
1	3	9	22.5	18.1
4	3	9	144.5	158.2
7	3	9	58.7	63.0
10	3	9	11.0	9.2
13	3	9	41.2	46.3
16	3	9	10.5	8.0
19	3	9	29.0	25.9
2	4	9	11.0	7.2
5	4	9	23.7	26.5
8	4	9	13.1	5.7
11	4	9	18.6	18.5
14	4	9	23.2	19.3
17	4	9	32.3	32.2
20	4	9	17.3	15.6
23	4	9	38.9	42.9
26	4	9	17.8	13.6
1	5	9	11.9	10.4
4	5	9	40.8	41.0
7	5	9	3.9	0.1
10	5	9	11.9	10.4
13	5	9	19.0	17.0
16	5	9	19.0	19.7
19	5	9	30.9	32.1
22	5	9	9.6	9.4
25	5	9	10.5	11.3
28	5	9	17.6	13.0
0	6	9	32.6	34.1
3	6	9	6.8	7.9
6	6	9	13.2	14.4
9	6	9	30.7	37.9
12	6	9	47.4	51.0
15	6	9	58.1	53.9
18	6	9	18.3	17.7
21	6	9	13.1	13.5
24	6	9	12.7	11.3
27	6	9	41.3	43.3
30	6	9	19.2	25.8
3	7	9	13.7	13.9
6	7	9	23.8	20.7
9	7	9	4.4	0.4
12	7	9	69.4	78.3
15	7	9	43.6	51.9
18	7	9	44.8	39.3
21	7	9	44.5	37.7
24	7	9	20.6	17.9
27	7	9	34.7	40.1
30	7	9	21.5	18.4
0	8	9	43.5	44.6
3	8	9	23.2	15.9
6	8	9	19.1	12.1
9	8	9	14.8	12.9
12	8	9	18.2	14.3
15	8	9	36.6	36.8
18	8	9	17.6	14.2
21	8	9	14.5	10.6
24	8	9	22.8	21.7
27	8	9	32.3	29.2
30	8	9	21.5	23.0
3	9	9	8.3	7.2
6	9	9	41.8	38.6
9	9	9	3.9	8.7
12	9	9	8.3	6.9
15	9	9	18.6	19.2
18	9	9	49.1	49.3
21	9	9	1.4	4.7
24	9	9	31.4	26.5
27	9	9	27.5	29.9
30	9	9	14.3	8.3
3	10	9	6.6	8.5
6	10	9	11.4	9.8
9	10	9	14.0	12.9
12	10	9	10.7	7.6
15	10	9	36.3	25.8
18	10	9	30.3	22.4
21	10	9	19.4	23.3
24	10	9	65.3	72.3
27	10	9	34.1	25.4
30	10	9	21.7	22.7
3	11	9	28.4	31.0
6	11	9	35.7	31.2
9	11	9	15.9	15.7
12	11	9	16.0	9.8
15	11	9	11.7	14.1
18	11	9	5.5	4.9
21	11	9	32.3	26.7
24	11	9	11.1	9.3
27	11	9	4.1	5.9
30	11	9	34.1	28.1
3	12	9	15.7	16.3
6	12	9	14.2	12.2
9	12	9	27.4	23.1
12	12	9	45.6	46.8
15	12	9	9.0	5.1
18	12	9	40.1	37.4
21	12	9	13.3	14.3
24	12	9	10.9	7.0
27	12	9	31.6	28.3
30	12	9	18.6	15.5
3	13	9	29.8	25.7
6	13	9	15.9	16.6
9	13	9	23.4	18.9
12	13	9	17.2	13.9
15	13	9	26.8	24.0
18	13	9	25.9	27.0
21	13	9	17.2	13.9
24	13	9	17.0	14.4
27	13	9	14.7	13.2
30	13	9	11.0	7.8
3	14	9	12.1	10.3
6	14	9	44.0	44.3
9	14	9	13.9	16.2
12	14	9	25.5	24.1
15	14	9	17.2	13.9
18	14	9	17.0	14.4
21	14	9	14.7	13.2
24	14	9	11.0	7.8
27	14	9	12.1	10.3
30	14	9	44.0	44.3
3	15	9	13.9	16.2
6	15	9	25.5	24.1
9	15	9	17.2	13.9
12	15	9	17.0	14.4
15	15	9	14.7	13.2
18	15	9	11.0	7.8
21	15	9	12.1	10.3
24	15	9	44.0	44.3
27	15	9	13.9	16.2
30	15	9	25.5	24.1
3	16	9	17.2	13.9
6	16	9	17.0	14.4
9	16	9	14.7	13.2
12	16	9	11.0	7.8
15	16	9	12.1	10.3
18	16	9	44.0	44.3
21	16	9	13.9	16.2
24	16	9	25.5	24.1
27	16	9	17.2	13.9
30	16	9	17.0	14.4
3	17	9	14.7	13.2
6	17	9	11.0	7.8
9	17	9	12.1	10.3
12	17	9	44.0	44.3
15	17	9	13.9	16.2
18	17	9	25.5	24.1
21	17	9	17.2	13.9
24	17	9	17.0	14.4
27	17	9	14.7	13.2
30	17	9	11.0	7.8
3	18	9	12.1	10.3
6	18	9	44.0	44.3
9	18	9	13.9	16.2
12	18	9	25.5	24.1
15	18	9	17.2	13.9
18	18	9	17.0	14.4
21	18	9	14.7	13.2
24	18	9	11.0	7.8
27	18	9	12.1	10.3
30	18	9	44.0	44.3
3	19	9	13.9	16.2
6	19	9	25.5	24.1
9	19	9	17.2	13.9
12	19	9	17.0	14.4
15	19	9	14.7	13.2
18	19	9	11.0	7.8
21	19	9	12.1	10.3
24	19

TABLE 1.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X'	Y'	Z
S(1)	6.320 ± 2	-1.504 ± 2	7.091 ± 1
C(2)	5.312 ± 5	-0.116 ± 5	6.460 ± 5
C(3)	6.239 ± 5	0.787 ± 4	5.643 ± 5
C(4)	6.874 ± 4	0.210 ± 4	4.334 ± 5
C(5)	8.517 ± 6	-1.582 ± 6	3.652 ± 6
C(6)	9.167 ± 6	-2.813 ± 7	3.826 ± 6
C(7)	8.910 ± 6	-3.595 ± 6	4.916 ± 6
C(8)	8.019 ± 6	-3.144 ± 6	5.873 ± 6
C(9)	7.346 ± 4	-1.917 ± 5	5.739 ± 5
C(10)	7.556 ± 4	-1.115 ± 5	4.621 ± 5
C(11)	5.833 ± 4	0.078 ± 4	3.230 ± 5
C(12)	5.128 ± 5	1.217 ± 5	2.825 ± 5
C(13)	4.158 ± 5	1.161 ± 5	1.813 ± 5
C(14)	3.873 ± 5	-0.034 ± 5	1.213 ± 5
C(15)	4.579 ± 5	-1.163 ± 5	1.540 ± 5
C(16)	5.548 ± 4	-1.109 ± 4	2.557 ± 5
C(17)	7.932 ± 5	1.271 ± 6	3.909 ± 6
C(18)	4.907 ± 7	0.664 ± 7	7.746 ± 6
C(19)	4.094 ± 5	-0.608 ± 6	5.728 ± 6
O(20)	2.920 ± 4	-0.128 ± 4	0.219 ± 4

TABLE 1.7

INTERBOND ANGLES AND E.S.D.S.

C(2) - S(1) - C(9)	103.7 ± 2°	C(7) - C(8) - C(9)	121.8 ± 5°
S(1) - C(2) - C(3)	107.4 ± 3	S(1) - C(9) - C(8)	114.5 ± 4
S(1) - C(2) - C(18)	103.8 ± 4	S(1) - C(9) - C(10)	125.0 ± 4
S(1) - C(2) - C(19)	111.5 ± 4	C(8) - C(9) - C(10)	120.5 ± 5
C(3) - C(2) - C(18)	107.6 ± 4	C(4) - C(10)- C(5)	117.1 ± 4
C(3) - C(2) - C(19)	115.1 ± 5	C(4) - C(10)- C(9)	126.0 ± 4
C(18)- C(2) - C(19)	110.8 ± 5	C(5) - C(10)- C(9)	117.0 ± 4
C(2) - C(3) - C(4)	118.3 ± 4	C(4) - C(11)- C(12)	118.9 ± 4
C(3) - C(4) - C(10)	110.2 ± 4	C(4) - C(11)- C(16)	124.3 ± 4
C(3) - C(4) - C(11)	111.1 ± 4	C(12)- C(11)- C(16)	116.8 ± 4
C(3) - C(4) - C(17)	104.7 ± 4	C(11)- C(12)- C(13)	121.7 ± 4
C(10)- C(4) - C(11)	111.6 ± 4	C(12)- C(13)- C(14)	119.7 ± 5
C(10)- C(4) - C(17)	109.9 ± 4	C(13)- C(14)- C(15)	120.5 ± 5
C(11)- C(4) - C(17)	109.0 ± 4	C(13)- C(14)- O(20)	121.3 ± 4
C(6) - C(5) - C(10)	120.6 ± 5	C(15)- C(14)- O(20)	118.1 ± 4
C(5) - C(6) - C(7)	120.9 ± 6	C(14)- C(15)- C(16)	119.7 ± 4
C(6) - C(7) - C(8)	119.1 ± 5	C(11)- C(16)- C(15)	121.5 ± 4

TABLE 1.8

INTERMOLECULAR CONTACTS BELOW 4 Å

O(20)....O(20)	ii	2.96 Å	C(14)....O(20)	ii	3.87 Å
C(13)....O(20)	iv	3.54	C(5).....C(13)	vii	3.87
C(15)....C(18)	iii	3.55	C(8).....C(6)	vi	3.88
C(14)....O(20)	iv	3.69	C(6).....C(15)	vi	3.88
S(1).....C(12)	iii	3.70	C(8).....C(7)	vi	3.88
C(7).....C(16)	vi	3.70	C(7).....C(6)	vi	3.89
C(5).....C(12)	vii	3.75	C(15)....O(20)	ii	3.95
C(6).....C(13)	vii	3.77	C(5).....C(17)	vii	3.96
C(17)....C(7)	v	3.78	C(5).....C(11)	vii	3.97
C(16)....C(18)	iii	3.82	S(1).....C(17)	viii	3.97
C(16)....C(17)	vii	3.83	C(15)....C(17)	vii	3.99
C(6).....C(12)	vii	3.84	C(18)....O(20)	i	3.99
C(7).....C(15)	vi	3.87	S(1).....C(3)	viii	4.00

Roman numerals refer to the transformations of the fractional coordinates given in Table 1.2.

i	$x, \quad y, \quad 1 + z;$		v	$\frac{1}{3} + y, \quad \frac{2}{3} + y - x, \quad \frac{2}{3} - z;$	
ii	$y, \quad y - x, \quad -z;$		vi	$\frac{2}{3} + y - x, \quad \frac{1}{3} - x, \quad \frac{1}{3} + z;$	
iii	$y, \quad y - x, \quad 1 - z;$		vii	$\frac{2}{3} - x, \quad \frac{1}{3} - y, \quad \frac{1}{3} - z;$	
iv	$x - y, \quad x, \quad -z;$		viii	$\frac{2}{3} - x, \quad \frac{1}{3} - y, \quad 1\frac{1}{3} - z;$	

The transformations are applied to the coordinates of the second atom in each case.

TABLE 1.9

MEAN MOLECULAR PLANES

(A) ATOMS DEFINING PLANES

PLANE NO.	ATOMS DEFINING PLANE
1	C(5), C(6) and C(7)
2	S(1), C(4), C(9) and C(10)
3	S(1), C(4), C(5), C(6), C(7), C(8), C(9) and C(10)
4	C(4), C(11), C(12), C(13), C(14), C(15), C(16) and O(20)

(B) PLANE EQUATIONS

PLANE NO.	P	Q	R	S	RMS D
1	-0.7496	-0.4506	-0.4849	-7.4421	0.000
2	-0.7597	-0.4695	-0.4498	-7.2784	0.013
3	-0.7479	-0.4693	-0.4695	-7.3058	0.029
4	0.6975	0.2060	-0.6863	1.8776	0.015

P, Q and R are the direction cosines of the plane normal, S is the plane to origin distance and RMS D is the root mean square deviation of the atoms defining the plane, from the plane, in Angstroms. The plane equation is then

$$PX + QY + RZ = S$$

where X, Y and Z are coordinates in Angstroms referred to standard orthogonal axes.

(C) DEVIATIONS FROM PLANES (Å)

PLANE NO. / ATOM	1	2	3	4
S(1)	-0.056	-0.007	-0.044	-2.646
C(2)	-	0.392	0.355	-2.630
C(3)	-	-0.369	-0.379	-1.237
C(4)	0.093	0.008	0.032	-0.014
C(5)	0.000	-	-0.036	1.231
C(6)	0.000	-	0.027	-0.962
C(7)	0.000	-	0.022	0.223
C(8)	-0.017	-	-0.026	1.312
C(9)	0.017	0.017	0.018	-1.087
C(10)	-0.039	-0.018	0.008	-0.009
C(11)	-	1.357	1.390	-0.010
C(12)	-	-	1.573	0.011
C(13)	-	-	2.800	0.018
C(14)	-	-	3.856	-0.016
C(15)	-	-	3.704	0.020
C(16)	-	-	2.476	0.009
C(17)	-	-1.103	-1.058	1.234
C(18)	-	-0.245	-0.312	-3.634
C(19)	-	1.877	1.840	-3.078
O(20)	-	-	5.080	-0.017

(D) DIHEDRAL ANGLES

PLANE A	PLANE B	∠ AB
1	2	2.4°
1	3	1.4
1	4	73.6
2	3	1.3
2	4	71.5
3	4	72.8

1.4 Discussion

The analysis was undertaken to determine the molecular structure of the ethanol included clathrate formed by the thia-analogue of Dianin's compound, 4-p-hydroxyphenyl-2,2,4-trimethyl-thiachroman in so far as this defines the nature of the cavity formed by Dianin's compound and related clathrates. The conformation of the host molecule together with that of 4-p-hydroxyphenyl-2,2,4-trimethylchroman (Dianin's compound) is discussed in Chapter 3.

The structure makes use of a crystallographic three-fold inversion axis. The essential feature of the structure is the linking of the hydroxy groups of six molecules by a network of hydrogen bonds such that the oxygen atoms form a distorted hexagon of radius 2.96 Å. Three of the oxygen atoms come from molecules of one configuration which lie below the hexagon, and three from molecules of the opposite configuration which lie above the hexagon.

Two such groups of six molecules are stacked along the c-axis forming a cage capable of entrapping one or more guest molecules. The top and bottom of the cage are formed by hexagons of oxygen atoms which are a unit translation apart in the direction of the c-axis. Thus the length of the cavity is 10.90 Å. The walls of the cage are formed by six molecules, three of one configuration are involved in hydrogen bonding at the lower end of the cage and the

remaining three of the other configuration are involved in hydrogen bonding at the upper end of the cage. The six molecules comprising the cage are bound at approximately $z = \frac{1}{2}$ by van der Waals' forces between the C(19) atoms of the gem-dimethyl groups which point into the cavity forming a waist of radius 4.16 Å.

By taking into account the van der Waals' volumes of the atoms comprising the cage, the space available within the cavity may be ascertained. This has an approximate hourglass shape in which the waist of approximate diameter 4 Å effectively separates the cavity into two halves, 6.4 Å in width at their point of widest extension.

Since the contents of the cavity will exhibit the symmetry of the cavity, namely $\bar{3}$ (C_{3i}), and since the ethanol molecules do not possess this symmetry, the ethanol molecules included within the cavity are triply disordered. In addition, the space available within the cavity at its point of widest extension is considerably greater than the van der Waals' volume of the ethanol molecule. Thus the host-guest interaction is small and it is probable that the two ethanol molecules are not rigidly fixed within the cavity but have considerable librational motion at room temperature. It is therefore not possible on this basis to define unambiguously the relative orientation of the ethanol molecules within the cavity. However the peaks observed in the difference synthesis of the cavity suggest that the ethanol molecules are located in the region

of the cavity having the largest cross-sectional area.

This is in general agreement with the results found by Flippen, Karle and Karle, (1970) in their analysis of 4-p-hydroxyphenyl-2,2,4-trimethylchroman (Dianin's compound).

Chapter 2

The Crystal and Molecular Structure of 2,5,5-Trimethylhex-3-yn-2-ol Included 4-*p*-Hydroxyphenyl-2,2,4-trimethylthiachroman

2.1 Experimental

Crystal Data

Host: 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman

Guest: 2,5,5-trimethylhex-3-yn-2-ol

Host:Guest :: 6:1

6 $C_{18}H_{20}OS$: $C_9H_{16}O$ F.W. = 307.8

Trigonal, a = 27.91 Å, c = 10.99 Å, (referred to hexagonal axes)

U = 7412 $Å^3$ F(000) = 2970 electrons

D_m = 1.24 $g.cm.^{-3}$ Z = 18 D_x = 1.241 $g.cm.^{-3}$

Space group: $R\bar{3}$ (C_{3i}^2, No. 148)

Linear absorption coefficient (Cu $K\alpha$, λ = 1.5418 Å) = 17 $cm.^{-1}$

The crystals used in this analysis were supplied by Dr. D.D. MacNicol. They consisted of colourless hexagonal needles elongated along the c-axis. Unit cell dimensions were obtained from rotation and Weissenberg photographs taken about the c-axis (Cu $K\alpha$ radiation, λ = 1.5418 Å). Since the crystals are isomorphous with the ethanol included clathrate of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman, the space group is $R\bar{3}$ (No. 148).

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the hki0,...hki9 reciprocal lattice nets taken with Cu $K\alpha$ radiation. The multiple film technique of Robertson, (1943) was used. The observed

intensities were reduced to structure amplitudes by applying the appropriate Lorentz, polarisation and rotation factors (Tunell, 1939). 2387 independent structure amplitudes (Table 2.4) were obtained, which represents 63 % of the data accessible to Cu $K\alpha$ radiation. No absorption corrections were applied.

The data were placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

2.2 Solution and Refinement of the Structure

The unit cell parameters of the 2,5,5-trimethylhex-3-yn-2-ol included clathrate of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman do not differ significantly from those of the ethanol included clathrate of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman. Thus the two host molecular structures are strictly isomorphous.

A set of phase angles based on the coordinates of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman from a previous analysis (Table 1.2) were used in conjunction with the observed structure amplitudes to evaluate an electron density synthesis. The coordinates of the atoms of the host molecule were obtained from this initial electron density synthesis. Successive cycles of Fourier refinement reduced the residual R from 0.277, based on the coordinates of the host molecule from the ethanol included clathrate, to 0.243, based on the coordinates of the host molecule from the 2,5,5-trimethylhex-3-yn-2-ol included clathrate.

The structure was then refined in eleven cycles of least-squares minimisation of the function $M = \sum w(|F_o| - |F_c|)^2$. D.R. Pollard's least-squares program, (1968) was used in the initial stages of the refinement. Three positional and one isotropic thermal parameters for each atom of the host molecule and an individual scale factor for each reciprocal lattice net were refined. Three consecutive cycles of refinement, in which the observations were

given unit weights and the full matrix of the normal equations was evaluated, reduced the R-factor to 0.186.

An electron density and difference synthesis of the cavity were calculated using the coordinates of the host molecule obtained in the final cycle of isotropic least-squares refinement. Both syntheses revealed three, and only three, independent peaks. Two were situated along the c-axis and the third was a general peak. Together with the $\bar{3}$ symmetry of the cavity these peaks give the unambiguous position of the guest molecule within the cavity.

A further three cycles of isotropic least-squares refinement, in which the coordinates of the guest molecule were included, reduced the R-factor to 0.143. The atoms co-linear with the c-axis were assigned occupation numbers of one third. A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 5/|F_o|_{max}$ was applied and a further cycle of isotropic least-squares refinement lowered the R-factor to 0.139.

On the assumption that the data were now on the same relative scale, the isotropic thermal parameters of the atoms of the host and guest molecules were replaced by six anisotropic temperature factors and individual scale factors by one overall scale factor. The atoms co-linear with the c-axis were assigned occupation

numbers equal to one third. Since these atoms are in special positions with respect to the space group symmetry, the values taken by their anisotropic temperature factors are restricted. There are, in consequence, only two independent anisotropic temperature factors (U_{ij}), namely U_{11} and U_{33}. The restrictions are that

$$U_{11} = U_{22} = 2U_{12} \qquad \text{and} \qquad 2U_{23} = 2U_{31} = 0.$$

The refinement was continued using the Glasgow S.F.L.S. program (Cruickshank and Smith, 1965). Convergence was achieved in a further four cycles of refinement, in which the block diagonal approximation to the matrix of the normal equations was used. The R-factor at the conclusion of the refinement was 0.099. The weighting scheme applied in the last four cycles of refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$$

where $p_1 = 5$, $p_2 = 0.01$ and $p_3 = 0.001$. The course of the refinement is summarised in Table 2.1.

The fractional atomic coordinates and anisotropic temperature factors of the host and guest molecules together with their estimated standard deviations are contained in Tables 2.2 and 2.3 respectively. The observed and final calculated structure amplitudes are given in Table 2.4. Atomic coordinates, in Angstroms, referred to orthogonal axes defined by X' parallel to $\underline{a}^*$, Y' normal

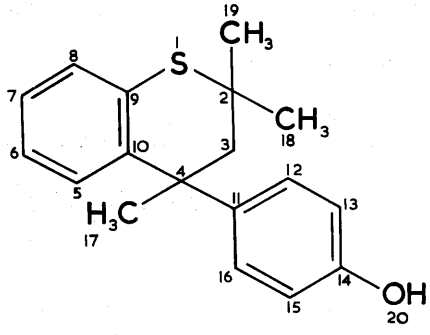
to a* and c and Z parallel to c are given in Table 2.5. Tables 2.6 and 2.7 contain the bond lengths and interbond angles of the host molecule together with their estimated standard deviations. The host-host intermolecular contacts below 4 Å are given in Table 2.8. Tables 2.9 and 2.10 contain the bond lengths and interbond angles of the guest molecule together with their estimated standard deviations. Table 2.11 contains the host-guest intermolecular contacts which are less than 4 Å. Estimated standard deviations, where quoted, are in units of the last decimal place of the quantity to which they refer.

The numbering of the atoms in the host and guest molecules is illustrated in Fig. 2.1. In Fig. 2.2, the structure is shown projected on (010), showing the guest molecule (II) within the cavity. Two molecules of the host (I), which lie directly above and below the cavity as viewed in this direction, have been excluded apart from their hydroxyl oxygen atoms. In Fig. 2.3 superimposed Fourier sections at z = 0.275 (full lines) and z = 0.725 (broken lines), contoured at intervals of approximately 1 e/Å^3, showing the staggered conformation of (II) are illustrated. The van der Waals' contacts of the host and guest, as viewed along the c-axis, is shown in Fig. 2.4. In the section shown at z = 0.275, the broken lines represent the van der Waals' volumes of the atoms comprising the cage and the full lines the approximate van der Waals' volumes of the guest.

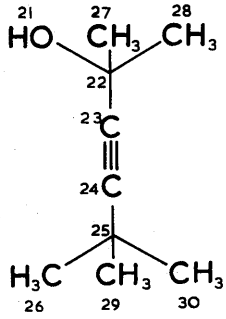
TABLES AND DIAGRAMS

FIGURE 2.1

The numbering of the non-hydrogen atoms of the host and guest molecules.


19
CH3
1
S
8
7
9
2
CH3
18
6
10
3
4
12
5
11
13
H3C
17
16
14
OH
20
15

I


21
HO
27
CH3
28
CH3
22
23
C
24
C
25
H3C
CH3
CH3
26
29
30

II

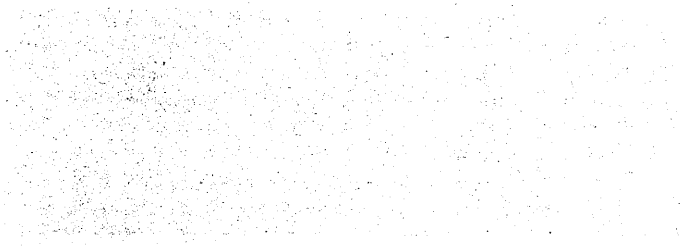


FIGURE 2.2

The packing of the host and guest molecules as projected on (010). Two molecules of the host, which lie directly above and below the cavity as viewed in this direction, have been excluded apart from their hydroxyl oxygen atoms.

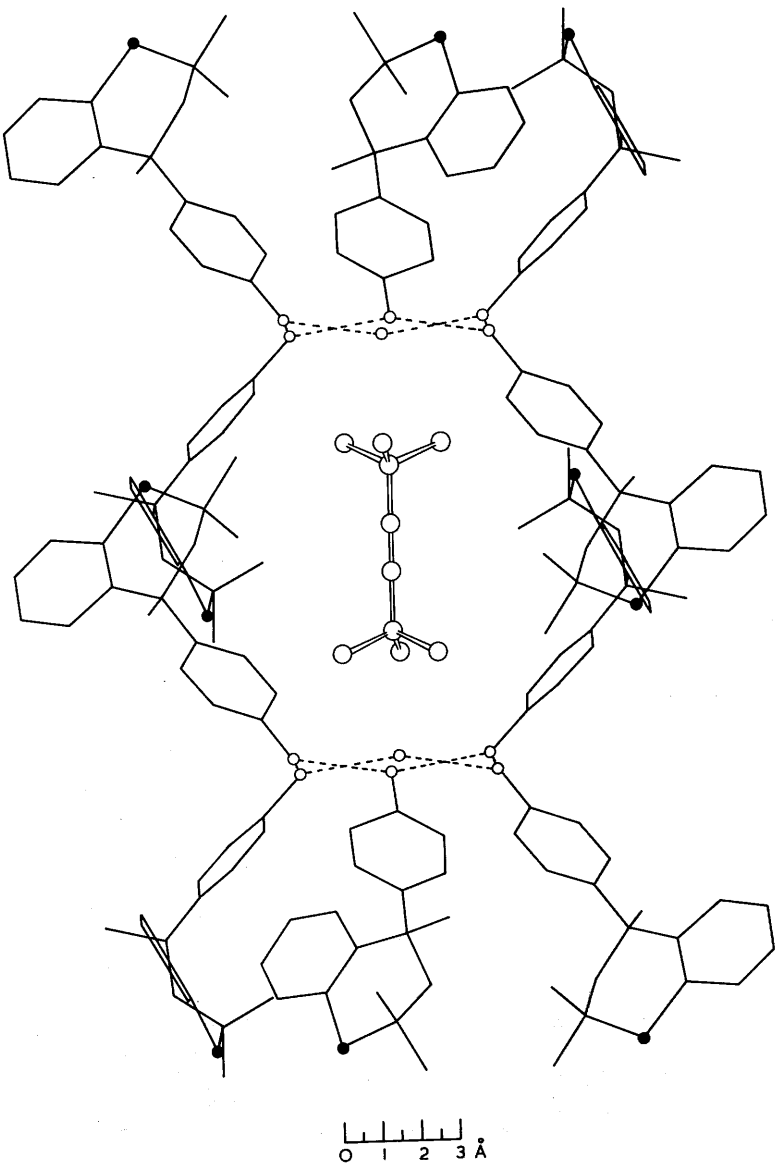

0 1 2 3 Å

FIGURE 2.3

Superimposed Fourier sections of the cavity at $z = 0.275$ (full lines) and $z = 0.725$ (broken lines), contoured at intervals of approximately 1 $e/\text{Å}^3$.

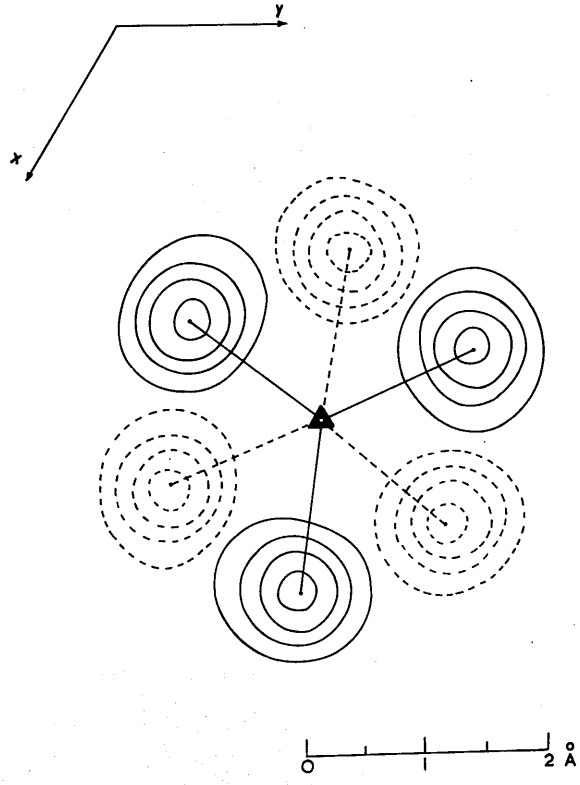

y
x
0
1
2 Å

FIGURE 2.4

The van der Waals' contacts of the host and guest at z = 0.275 as viewed along the c-axis. The broken lines represent the van der Waals' volumes of the atoms comprising the cage and the full lines the approximate van der Waals' volumes of the guest.

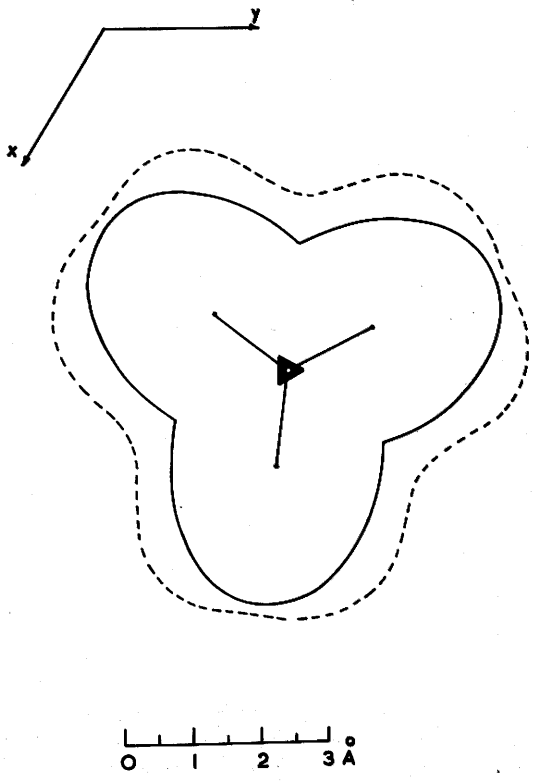

y
x
0 1 2 3 Å

TABLE 2.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	S + 18 C + O	0.277
2	S + 18 C + O	0.254
3	S + 18 C + O	0.243

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layer scales, unit weights; host molecule alone	0.207
2	"	0.193
3	"	0.186
4	As above, guest molecule included	0.157
5	"	0.146
6	"	0.143
7	As above, weighting scheme 1 applied	0.139
8	Block diagonal, individual anisotropic temperature factors, overall scale factor, weighting scheme 2 applied	0.117
9	"	0.103
10	"	0.100
11	"	0.099

TABLE 2.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
S(1)	0.2639 ± 1	0.0771 ± 1	0.6481 ± 2
C(2)	0.2237 ± 2	0.1069 ± 2	0.5913 ± 5
C(3)	0.2610 ± 2	0.1576 ± 2	0.5145 ± 5
C(4)	0.2869 ± 2	0.1499 ± 2	0.3982 ± 5
C(5)	0.3528 ± 3	0.1178 ± 3	0.3360 ± 7
C(6)	0.3798 ± 3	0.0874 ± 4	0.3491 ± 8
C(7)	0.3697 ± 3	0.0548 ± 3	0.4513 ± 8
C(8)	0.3332 ± 3	0.0528 ± 3	0.5361 ± 7
C(9)	0.3060 ± 2	0.0828 ± 2	0.5245 ± 6
C(10)	0.3153 ± 2	0.1162 ± 2	0.4207 ± 6
C(11)	0.2437 ± 2	0.1246 ± 2	0.2956 ± 5
C(12)	0.2155 ± 3	0.1510 ± 2	0.2562 ± 6
C(13)	0.1761 ± 3	0.1300 ± 3	0.1654 ± 6
C(14)	0.1638 ± 2	0.0808 ± 2	0.1087 ± 5
C(15)	0.1909 ± 3	0.0534 ± 2	0.1439 ± 6
C(16)	0.2304 ± 2	0.0751 ± 2	0.2364 ± 5
C(17)	0.3305 ± 3	0.2090 ± 3	0.3586 ± 6
C(18)	0.2068 ± 3	0.1264 ± 3	0.7057 ± 7
C(19)	0.1720 ± 3	0.0632 ± 3	0.5266 ± 6
O(20)	0.1242 ± 2	0.0579 ± 2	0.0197 ± 4

C(21)	0.0218 ± 8	0.0578 ± 5	0.2650 ± 15
C(22)	0.0000 ± 0	0.0000 ± 0	0.3127 ± 14
C(23)	0.0000 ± 0	0.0000 ± 0	0.4426 ± 16

TABLE 2.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
S(1)	0.0683 10	0.0735 11	0.0346 10	0.0435 15	0.0230 14	0.0681 17
C(2)	0.0569 34	0.0548 33	0.0244 35	-0.0056 46	0.0064 47	0.0444 56
C(3)	0.0686 38	0.0510 32	0.0228 35	-0.0145 45	-0.0055 49	0.0542 58
C(4)	0.0528 31	0.0491 30	0.0277 33	0.0019 44	-0.0022 46	0.0494 51
C(5)	0.0645 40	0.1036 55	0.0344 42	-0.0165 67	-0.0071 57	0.1037 82
C(6)	0.0674 44	0.1094 63	0.0477 48	-0.0240 78	-0.0184 66	0.1028 89
C(7)	0.0703 44	0.0916 53	0.0635 52	-0.0328 78	-0.0328 71	0.1032 85
C(8)	0.0793 47	0.0684 43	0.0559 47	-0.0071 67	-0.0359 69	0.0918 78
C(9)	0.0514 32	0.0502 32	0.0384 38	-0.0069 47	-0.0141 49	0.0440 53
C(10)	0.0495 31	0.0594 35	0.0272 34	-0.0061 47	-0.0116 46	0.0491 54
C(11)	0.0559 32	0.0512 31	0.0211 32	0.0035 43	0.0020 43	0.0569 51
C(12)	0.0689 38	0.0556 35	0.0378 38	-0.0065 50	-0.0068 54	0.0783 61
C(13)	0.0702 39	0.0648 38	0.0331 37	0.0021 53	-0.0015 53	0.0855 67

C(14)	0.0571 33	0.0665 36	0.0182 32	-0.0085 47	-0.0119 45	0.0630 58
C(15)	0.0665 37	0.0597 36	0.0306 36	-0.0152 51	-0.0133 51	0.0719 62
C(16)	0.0622 34	0.0597 34	0.0229 34	-0.0098 46	-0.0017 46	0.0759 58
C(17)	0.0658 40	0.0627 40	0.0355 41	0.0181 56	0.0051 57	0.0343 64
C(18)	0.0957 57	0.0810 51	0.0397 46	-0.0100 69	0.0305 74	0.0807 89
C(19)	0.0576 38	0.0713 42	0.0399 42	-0.0196 60	0.0028 57	0.0402 66
O(20)	0.0790 32	0.0842 33	0.0337 28	-0.0143 45	-0.0423 43	0.0863 54
C(21)	0.1607 154	0.0987 85	0.0995 99	0.0258 141	-0.0552 194	0.1153 185
C(22)	0.0740 59	0.0740 59	0.0487 91	0.0000 0	0.0000 0	0.0166 59
C(23)	0.0836 65	0.0836 65	0.0472 76	0.0000 0	0.0000 0	0.0231 65

TABLE 2.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES

H	K	L	F OBS	F CALC
4	1	0	42.5	59.2
7	1	0	109.5	97.4
10	1	0	167.8	153.2
13	1	0	29.6	7.0
16	1	0	85.6	83.3
19	1	0	31.8	27.5
22	1	0	26.0	27.2
25	1	0	13.6	19.7
2	2	0	219.1	255.1
5	2	0	200.2	169.8
8	2	0	104.0	116.7
11	2	0	28.0	12.2
17	2	0	11.7	10.9
20	2	0	10.3	9.6
29	2	0	20.7	22.5
0	3	0	172.9	179.4
3	3	0	359.4	359.1
6	3	0	148.3	132.3
9	3	0	23.1	31.9
12	3	0	62.8	72.4
15	3	0	6.4	13.7
18	3	0	26.0	26.8
21	3	0	82.9	81.7
24	3	0	32.0	30.1
27	3	0	20.9	26.9
1	4	0	124.5	148.0
4	4	0	107.6	120.8
10	4	0	114.1	100.3
13	4	0	104.9	112.3
16	4	0	8.3	5.9
19	4	0	53.6	59.5
22	4	0	44.1	46.6
25	4	0	15.8	27.8
28	4	0	6.3	12.9
2	5	0	245.2	227.5
5	5	0	11.2	12.9
8	5	0	6.4	4.8
11	5	0	44.2	58.0
14	5	0	48.5	46.8
17	5	0	17.5	24.8
20	5	0	26.5	22.4
26	5	0	26.7	35.7
0	6	0	164.8	186.9
3	6	0	49.2	49.2
6	6	0	50.4	24.9
9	6	0	16.1	9.0
12	6	0	23.0	19.6
15	6	0	50.7	48.0
18	6	0	26.9	22.6
24	6	0	21.8	23.7
27	6	0	6.7	10.0
1	7	0	29.3	53.5
4	7	0	158.5	188.8
7	7	0	15.2	14.8
10	7	0	19.0	18.2
16	7	0	7.2	14.3
25	7	0	32.6	33.0
2	8	0	161.8	146.1
5	8	0	155.8	136.2
8	8	0	8.4	19.6
11	8	0	39.2	43.6
17	8	0	30.2	37.3
20	8	0	49.5	57.9
23	8	0	11.8	12.5
0	9	0	60.0	44.9
3	9	0	70.0	61.8
6	9	0	20.5	15.0
9	9	0	194.9	188.0
18	9	0	10.2	4.6
21	9	0	17.0	23.3
24	9	0	18.3	26.0
1	10	0	119.2	121.0
4	10	0	65.9	39.0
7	10	0	54.8	52.2
10	10	0	24.1	25.6
13	10	0	101.6	96.5
16	10	0	26.1	20.2
22	10	0	9.0	4.7
2	11	0	147.9	124.5
5	11	0	20.0	12.8
8	11	0	20.5	15.9
11	11	0	85.9	95.0
14	11	0	39.6	31.0
17	11	0	23.2	29.9
23	11	0	7.2	10.0
0	12	0	32.0	33.0
3	12	0	24.9	20.2
6	12	0	59.9	53.4
9	12	0	35.3	33.2
12	12	0	62.5	47.3
15	12	0	16.2	16.4
1	13	0	15.0	13.7
4	13	0	101.4	95.0
7	13	0	96.6	98.4
13	13	0	48.6	34.4
16	13	0	9.1	9.3
19	13	0	36.4	42.8
22	13	0	7.0	10.1
2	14	0	19.0	10.3
5	14	0	37.7	31.4
11	14	0	12.7	4.7
14	14	0	27.2	23.8
17	14	0	11.7	18.3
20	14	0	22.7	27.2
0	15	0	112.8	121.2
3	15	0	71.7	70.9
9	15	0	57.7	42.1
12	15	0	20.8	25.2
15	15	0	13.2	11.5
1	16	0	18.2	5.9
4	16	0	13.3	13.2
10	16	0	50.3	57.0
13	16	0	24.4	19.5
16	16	0	10.5	12.4
19	16	0	7.4	9.1
2	17	0	85.6	66.7
8	17	0	28.2	23.1
11	17	0	38.3	25.0
0	18	0	28.5	33.1
3	18	0	30.2	35.3
6	18	0	50.3	45.4
9	18	0	40.4	43.5
12	18	0	8.7	8.8
15	18	0	7.0	11.6
1	19	0	41.0	40.4
4	19	0	21.0	15.7
7	19	0	20.9	22.7
10	19	0	46.6	46.8
13	19	0	20.2	20.8
16	19	0	6.1	9.0
2	20	0	12.6	11.8
5	20	0	12.1	10.2
8	20	0	65.1	58.6
H	K	L	F OBS	F CALC
11	20	0	42.5	59.2
14	20	0	109.5	97.4
0	21	0	167.8	153.2
12	21	0	29.6	7.0
1	22	0	85.6	83.3
10	22	0	31.8	27.5
13	22	0	26.0	27.2
5	23	0	13.6	19.7
11	23	0	219.1	255.1
6	24	0	200.2	169.8
9	24	0	104.0	116.7
4	25	0	28.0	12.2
2	26	0	11.7	10.9
5	26	0	10.3	9.6
8	26	0	20.7	22.5
0	27	0	172.9	179.4
3	27	0	359.4	359.1
6	27	0	148.3	132.3
1	28	0	23.1	31.9
4	28	0	62.8	72.4
2	29	0	6.4	13.7
0	30	0	26.0	26.8
4	0	1	82.9	81.7
7	0	1	32.0	30.1
10	0	1	20.9	26.9
13	0	1	124.5	148.0
16	0	1	107.6	120.8
19	0	1	114.1	100.3
22	0	1	104.9	112.3
2	1	1	8.3	5.9
5	1	1	53.6	59.5
8	1	1	44.1	46.6
11	1	1	15.8	27.8
14	1	1	6.3	12.9
3	2	1	245.2	227.5
6	2	1	11.2	12.9
9	2	1	6.4	4.8
12	2	1	44.2	58.0
15	2	1	48.5	46.8
18	2	1	17.5	24.8
21	2	1	26.5	22.4
27	2	1	26.7	35.7
1	3	1	164.8	186.9
4	3	1	49.2	49.2
7	3	1	50.4	24.9
10	3	1	16.1	9.0
13	3	1	23.0	19.6
16	3	1	50.7	48.0
19	3	1	26.9	22.6
22	3	1	21.8	23.7
25	3	1	6.7	10.0
2	4	1	29.3	53.5
5	4	1	158.5	188.8
8	4	1	15.2	14.8
11	4	1	19.0	18.2
17	4	1	7.2	14.3
26	4	1	32.6	33.0
1	5	1	161.8	146.1
4	5	1	155.8	136.2
7	5	1	8.4	19.6
10	5	1	39.2	43.6
16	5	1	30.2	37.3
19	5	1	49.5	57.9
22	5	1	11.8	12.5
1	6	1	60.0	44.9
4	6	1	70.0	61.8
7	6	1	20.5	15.0
10	6	1	194.9	188.0
13	6	1	10.2	4.6
16	6	1	17.0	23.3
19	6	1	18.3	26.0
0	7	1	119.2	121.0
3	7	1	65.9	39.0
6	7	1	54.8	52.2
9	7	1	24.1	25.6
12	7	1	101.6	96.5
15	7	1	26.1	20.2
21	7	1	9.0	4.7
1	8	1	147.9	124.5
4	8	1	20.0	12.8
7	8	1	20.5	15.9
10	8	1	85.9	95.0
13	8	1	39.6	31.0
16	8	1	23.2	29.9
22	8	1	7.2	10.0
1	9	1	32.0	33.0
4	9	1	24.9	20.2
7	9	1	59.9	53.4
10	9	1	35.3	33.2
13	9	1	62.5	47.3
16	9	1	16.2	16.4
1	10	1	15.0	13.7
7	10	1	101.4	95.0
10	10	1	96.6	98.4
13	10	1	48.6	34.4
16	10	1	9.1	9.3
19	10	1	36.4	42.8
22	10	1	7.0	10.1
2	11	1	19.0	10.3
5	11	1	37.7	31.4
11	11	1	12.7	4.7
14	11	1	27.2	23.8
17	11	1	11.7	18.3
20	11	1	22.7	27.2
0	12	1	112.8	121.2
3	12	1	71.7	70.9
9	12	1	57.7	42.1
12	12	1	20.8	25.2
15	12	1	13.2	11.5
1	13	1	18.2	5.9
4	13	1	13.3	13.2
10	13	1	50.3	57.0
13	13	1	24.4	19.5
16	13	1	10.5	12.4
19	13	1	7.4	9.1
2	14	1	85.6	66.7
8	14	1	28.2	23.1
11	14	1	38.3	25.0
0	15	1	28.5	33.1
3	15	1	30.2	35.3
6	15	1	50.3	45.4
9	15	1	40.4	43.5
12	15	1	8.7	8.8
15	15	1	7.0	11.6
1	16	1	41.0	40.4
4	16	1	21.0	15.7
7	16	1	20.9	22.7
10	16	1	46.6	46.8
13	16	1	20.2	20.8
16	16	1	6.1	9.0
2	17	1	12.6	11.8
5	17	1	12.1	10.2
8	17	1	65.1	58.6
H	K	L	F OBS	F CALC
11	17	1	42.5	59.2
14	17	1	109.5	97.4
0	18	1	167.8	153.2
13	18	1	29.6	7.0
1	19	1	85.6	83.3
10	19	1	31.8	27.5
13	19	1	26.0	27.2
5	20	1	13.6	19.7
11	20	1	219.1	255.1
6	21	1	200.2	169.8
9	21	1	104.0	116.7
4	22	1	28.0	12.2
2	23	1	11.7	10.9
5	23	1	10.3	9.6
8	23	1	20.7	22.5
0	24	1	172.9	179.4
3	24	1	359.4	359.1
6	24	1	148.3	132.3
9	24	1	23.1	31.9
12	24	1	62.8	72.4
15	24	1	6.4	13.7
18	24	1	26.0	26.8
21	24	1	82.9	81.7
24	24	1	32.0	30.1
27	24	1	20.9	26.9
1	25	1	124.5	148.0
4	25	1	107.6	120.8
10	25	1	114.1	100.3
13	25	1	104.9	112.3
16	25	1	8.3	5.9
19	25	1	53.6	59.5
22	25	1	44.1	46.6
25	25	1	15.8	27.8
28	25	1	6.3	12.9
2	26	1	245.2	227.5
5	26	1	11.2	12.9
8	26	1	6.4	4.8
11	26	1	44.2	58.0
14	26	1	48.5	46.8
17	26	1	17.5	24.8
20	26	1	26.5	22.4
26	26	1	26.7	35.7
0	27	1	164.8	186.9
3	27	1	49.2	49.2
6	27	1	50.4	24.9
9	27	1	16.1	9.0
12	27	1	23.0	19.6
15	27	1	50.7	48.0
18	27	1	26.9	22.6
24	27	1	21.8	23.7
27	27	1	6.7	10.0
1	28	1	29.3	53.5
4	28	1	158.5	188.8
7	28	1	15.2	14.8
10	28	1	19.0	18.2
16	28	1	7.2	14.3
25	28	1	32.6	33.0
2	29	1	161.8	146.1
5	29	1	155.8	136.2
8	29	1	8.4	19.6
11	29	1	39.2	43.6
17	29	1	30.2	37.3
20	29	1	49.5	57.9
23	29	1	11.8	12.5
0	30	1	60.0	44.9
3	30	1	70.0	61.8
6	30	1	20.5	15.0
9	30	1	194.9	188.0
18	30	1	10.2	4.6
21	30	1	17.0	23.3
24	30	1	18.3	26.0
1	31	1	119.2	121.0
4	31	1	65.9	39.0
7	31	1	54.8	52.2
10	31	1	24.1	25.6
13	31	1	101.6	96.5
16	31	1	26.1	20.2
22	31	1	9.0	4.7
2	32	1	147.9	124.5
5	32	1	20.0	12.8
8	32	1	20.5	15.9
11	32	1	85.9	95.0
14	32	1	39.6	31.0
17	32	1	23.2	29.9
23	32	1	7.2	10.0
0	33	1	32.0	33.0
3	33	1	24.9	20.2
6	33	1	59.9	53.4
9	33	1	35.3	33.2
12	33	1	62.5	47.3
15	33	1	16.2	16.4
1	34	1	15.0	13.7
4	34	1	101.4	95.0
7	34	1	96.6	98.4
13	34	1	48.6	34.4
16	34	1	9.1	9.3
19	34	1	36.4	42.8
22	34	1	7.0	10.1
2	35	1	19.0	10.3
5	35	1	37.7	31.4
11	35	1	12.7	4.7
14	35	1	27.2	23.8
17	35	1	11.7	18.3
20	35	1	22.7	27.2
0	36	1	112.8	121.2
3	36	1	71.7	70.9
9	36	1	57.7	42.1
12	36	1	20.8	25.2
15	36	1	13.2	11.5
1	37	1	18.2	5.9
4	37	1	13.3	13.2
10	37	1	50.3	57.0
13	37	1	24.4	19.5
16	37	1	10.5	12.4
19	37	1	7.4	9.1
2	38	1	85.6	66.7
8	38	1	28.2	23.1
11	38	1	38.3	25.0
0	39	1	28.5	33.1
3	39	1	30.2	35.3
6	39	1	50.3	45.4
9	39	1	40.4	43.5
12	39	1	8.7	8.8
15	39	1	7.0	11.6
1	40	1	41.0	40.4
4	40	1	21.0	15.7
7	40	1	20.9	22.7
10	40	1	46.6	46.8
13	40	1	20.2	20.8
16	40	1	6.1	9.0
2	41	1	12.6	11.8
5	41	1	12.1	10.2
8	41	1	65.1	58.6
H	K	L	F OBS	F CALC
11	41	1	42.5	59.2
14	41	1	109.5	97.4
0	42	1	167.8	153.2
13	42	1	29.6	7.0
1	43	1	85.6	83.3
10	43	1	31.8	27.5
13	43	1	26.0	27.2
5	44	1	13.6	19.7
11	44	1	219.1	255.1
6	45	1	200.2	169.8
9	45	1	104.0	116.7
4	46	1	28.0	12.2
2	47	1	11.7	10.9
5	47	1	10.3	9.6
8	47	1	20.7	22.5
0	48	1	172.9	179.4
3	48	1	359.4	359.1
6	48	1	148.3	132.3
1	49	1	23.1	31.9
4	49	1	62.8	72.4
2	50	1	6.4	13.7
0	51	1	26.0	26.8
4	1	2	82.9	81.7
7	1	2	32.0	30.1
10	1	2	20.9	26.9
13	1	2	124.5	148.0
16	1	2	107.6	120.8
19	1	2	114.1	100.3
22	1	2	104.9	112.3
2	2	2	8.3	5.9
5	2	2	53.6	59.5
8	2	2	44.1	46.6
11	2	2	15.8	27.8
14	2	2	6.3	12.9
3	3	2	245.2	227.5
6	3	2	11.2	12.9
9	3	2	6.4	4.8
12	3	2	44.2	58.0
15	3	2	48.5	46.8
18	3	2	17.5	24.8
21	3	2	26.5	22.4
27	3	2	26.7	35.7
1	4	2	164.8	186.9
4	4	2	49.2	49.2
7	4	2	50.4	24.9
10	4	2	16.1	9.0
13	4	2	23.0	19.6
16	4	2	50.7	48.0
19	4	2	26.9	22.6
22	4	2	21.8	23.7
25	4	2	6.7	10.0
2	5	2	29.3	53.5
5	5	2	158.5	188.8
8	5	2	15.2	14.8
11	5	2	19.0	18.2
17	5	2	7.2	14.3
26	5	2	32.6	33.0
1	6	2	161.8	146.1
4	6	2	155.8	136.2
7	6	2	8.4	19.6
10	6	2	39.2	43.6
16	6	2	30.2	37.3
19	6	2	49.5	57.9
22	6	2	11.8	12.5
1	7	2	60.0	44.9
4	7	2	70.0	61.8
7	7	2	20.5	15.0
10	7	2	194.9	188.0
13	7	2	10.2	4.6
16	7	2	17.0	23.3
19	7	2	18.3	26.0
0	8	2	119.2	121.0
3	8	2	65.9	39.0
6	8	2	54.8	52.2
9	8	2	24.1	25.6
12	8	2	101.6	96.5
15	8	2	26.1	20.2
21	8	2	9.0	4.7
1	9	2	147.9	124.5
4	9	2	20.0	12.8
7	9	2	20.5	15.9
10	9	2	85.9	95.0
13	9	2	39.6	31.0
16	9	2	23.2	29.9
22	9	2	7.2	10.0
1	10	2	32.0	33.0
4	10	2	24.9	20.2
7	10	2	59.9	53.4
10	10	2	35.3	33.2
13	10	2	62.5	47.3
16	10	2	16.2	16.4
1	11	2	15.0	13.7
4	11	2	101.4	95.0
7	11	2	96.6	98.4
13	11	2	48.6	34.4
16	11	2	9.1	9.3
19	11	2	36.4	42.8
22	11	2	7.0	10.1
2	12	2	19.0	10.3
5	12	2	37.7	31.4
11	12	2	12.7	4.7
14	12	2	27.2	23.8
17	12	2	11.7	18.3
20	12	2	22.7	27.2
0	13	2	112.8	121.2
3	13	2	71.7	70.9
9	13	2	57.7	42.1
12	13	2	20.8	25.2
15	13	2	13.2	11.5
1	14	2	18.2	5.9
4	14	2	13.3	13.2
10	14	2	50.3	57.0
13	14	2	24.4	19.5
16	14	2	10.5	12.4
19	14	2	7.4	9.1
2	15	2	85.6	66.7
8	15	2	28.2	23.1
11	15	2	38.3	25.0
0	16	2	28.5	33.1
3	16	2	30.2	35.3
6	16	2	50.3	45.4
9	16	2	40.4	43.5
12	16	2	8.7	8.8
15	16	2	7.0	11.6
1	17	2	41.0	40.4
4	17	2	21.0	15.7
7	17	2	20.9	22.7
10	17	2	46.6	46.8
13	17	2	20.2	20.8
16	17	2	6.1	9.0
2	18	2	12.6	11.8
5	18	2	12.1	10.2
8	18	2	65.1	58.6
H	K	L	F OBS	F CALC
11	18	2	42.5	59.2
14	18	2	109.5	97.4
0	19	2	167.8	153.2
13	19	2	29.6	7.0
1	20	2	85.6	83.3
10	20	2	31.8	27.5
13	20	2	26.0	27.2
5	21	2	13.6	19.7
11	21	2	219.1	255.1
6	22	2	200.2	169.8
9	22	2	104.0	116.7
4	23	2	28.0	12.2
2	24	2	11.7	10.9
5	24	2	10.3	9.6
8	24	2	20.7	22.5
0	25	2	172.9	179.4
3	25	2	359.4	359.1
6	25	2	148.3	132.3
1	26	2	23.1	31.9
4	26	2	62.8	72.4
2	27	2	6.4	13.7
0	28	2	26.0	26.8
4	2	2	82.9	81.7
7	2	2	32.0	30.1
10	2	2	20.9	26.9
13	2	2	124.5	148.0
16	2	2	107.6	120.8
19	2	2	114.1	100.3
22	2	2	104.9	112.3
2	3	2	8.3	5.9
5	3	2	53.6	59.5
8	3	2	44.1	46.6
11	3	2	15.8	27.8
14	3	2	6.3	12.9
3	4	2	245.2	227.5
6	4	2	11.2	12.9
9	4	2	6.4	4.8
12	4	2	44.2	58.0
15	4	2	48.5	46.8
18	4	2	17.5	24.8
21	4	2	26.5	22.4
27	4	2	26.7	35.7
1	5	2	164.8	186.9
4	5	2	49.2	49.2
7	5	2	50.4	24.9
10	5	2	16.1	9.0
13	5	2	23.0	19.6
16	5	2	50.7	48.0
19	5	2	26.9	22.6
22	5	2	21.8	23.7
25	5	2	6.7	10.0
2	6	2	29.3	53.5
5	6	2	158.5	188.8
8	6	2	15.2	14.8
11	6	2	19.0	18.2
17	6	2	7.2	14.3
26	6	2	32.6	33.0
1	7	2	161.8	146.1
4	7	2	155.8	136.2
7	7	2	8.4	19.6
10	7	2	39.2	43.6
16	7	2	30.2	37.3
19	7	2	49.5	57.9
22	7	2	11.8	12.5
1	8	2	60.0	44.9
4	8	2	70.0	61.8
7	8	2	20.5	15.0
10	8	2	194.9	188.0
13	8	2	10.2	4.6
16	8	2	17.0	23.3
19	8	2	18.3	26.0
0	9	2	119.2	121.0
3	9	2	65.9	39.0
6	9	2	54.8	52.2
9	9	2	24.1	25.6
12	9	2	101.6	96.5
15	9	2	26.1	20.2
21

H	K	L	F OBS	F CALC
19	7	1	41.0	53.3
22	7	1	12.6	15.1
25	7	1	7.2	14.1
2	8	1	175.5	155.7
5	8	1	152.0	121.9
8	8	1	27.9	30.2
11	8	1	129.8	119.6
14	8	1	71.2	65.3
17	8	1	9.9	12.1
0	9	1	9.9	4.4
3	9	1	16.0	10.9
9	9	1	193.4	148.9
12	9	1	44.6	41.3
15	9	1	14.0	20.4
18	9	1	14.3	10.4
24	9	1	16.1	21.3
4	10	1	214.4	204.5
7	10	1	94.8	92.5
10	10	1	22.4	24.2
13	10	1	40.4	31.1
19	10	1	19.7	19.4
5	11	1	11.3	15.2
8	11	1	21.8	27.7
11	11	1	140.6	127.2
17	11	1	36.9	31.1
20	11	1	21.8	21.4
0	12	1	24.0	13.5
3	12	1	62.9	36.4
6	12	1	36.8	36.2
9	12	1	60.1	49.1
12	12	1	32.0	31.0
15	12	1	22.1	26.7
18	12	1	12.6	9.4
21	12	1	6.1	9.6
1	13	1	12.9	10.9
4	13	1	96.1	95.2
7	13	1	41.6	39.4
13	13	1	41.7	43.6
19	13	1	12.9	13.7
2	14	1	11.1	17.3
14	14	1	14.8	9.7
20	14	1	11.2	13.3
0	15	1	71.8	79.9
6	15	1	60.9	59.0
9	15	1	34.3	29.8
15	15	1	12.1	12.1
1	16	1	11.8	20.0
4	16	1	37.5	36.6
10	16	1	13.0	7.2
2	17	1	41.2	33.1
5	17	1	53.0	55.4
8	17	1	28.4	25.9
11	17	1	40.8	31.8
14	17	1	30.5	31.7
17	17	1	7.3	9.9
0	18	1	28.1	19.3
3	18	1	20.7	14.9
6	18	1	42.0	51.0
9	18	1	24.0	18.6
12	18	1	20.6	24.8
1	19	1	21.5	17.1
4	19	1	13.1	22.9
7	19	1	27.6	32.8
10	19	1	15.2	16.3
2	20	1	17.9	23.5
5	20	1	8.4	11.2
11	20	1	14.9	22.5
14	20	1	8.4	6.0
3	21	1	20.9	19.9
6	21	1	18.5	19.2
12	21	1	20.4	19.8
1	22	1	39.0	39.3
10	22	1	16.5	17.9
2	23	1	34.6	33.4
5	23	1	36.5	38.5
8	23	1	12.4	14.8
11	23	1	7.5	15.6
0	24	1	31.7	29.5
3	24	1	10.9	29.2
6	24	1	5.3	1.4
1	25	1	6.2	15.1
4	25	1	11.5	6.1
7	25	1	11.0	14.7
2	26	1	21.4	22.7
0	27	1	13.0	13.0
-1	2	3	43.0	34.6
-1	5	3	8.1	17.2
-1	11	3	19.7	19.7
-1	14	3	92.4	84.6
-1	17	3	18.9	20.9
-1	20	3	41.3	44.2
-1	23	3	26.9	34.7
-1	29	3	6.6	6.9
-2	4	3	151.6	171.7
-2	7	3	199.8	174.6
-2	10	3	85.6	93.9
-2	13	3	8.6	19.7
-2	16	3	22.9	9.0
-2	22	3	22.7	35.2
-2	28	3	5.5	14.4
-3	1	3	95.9	98.2
-3	9	3	113.9	129.1
-3	12	3	127.6	137.7
-3	18	3	34.4	39.4
-3	21	3	13.8	24.4
-3	24	3	8.5	10.1
-3	27	3	29.3	31.1
-3	30	3	12.1	15.1
-4	5	3	126.6	127.4
-4	8	3	112.4	98.7
-4	11	3	48.4	44.7
-4	14	3	77.6	65.2
-4	17	3	20.4	18.0
-4	23	3	16.4	25.6
-4	26	3	59.7	65.1
-4	29	3	9.7	14.5
-5	7	3	75.0	94.3
-5	10	3	54.4	42.3
-5	13	3	178.3	191.2
-5	16	3	58.9	51.2
-5	19	3	36.0	44.0
-5	22	3	28.2	21.8
-5	25	3	18.3	24.2
-5	28	3	21.1	15.9
-6	31	3	3.1	12.6
-6	9	3	51.7	39.9
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-6	15	3	21.6	23.5
-6	18	3	17.9	10.1
-6	21	3	39.4	31.6
-6	24	3	47.0	46.8
-6	27	3	13.5	11.4
-7	4	3	98.2	95.0
-7	11	3	102.7	127.5
-7	14	3	26.5	34.3
-7	17	3	50.4	67.5
-7	20	3	37.4	51.6
-7	23	3	14.5	11.5
-7	26	3	9.8	18.5
-8	10	3	81.2	78.9
-8	13	3	197.5	178.4
-8	16	3	94.3	52.0
-8	19	3	20.4	22.1
-8	22	3	32.5	31.4
-8	25	3	46.8	35.3
-8	28	3	29.4	36.2
-9	31	3	11.3	18.2
-9	12	3	44.3	48.4
-9	15	3	73.7	79.2
-9	18	3	105.5	103.9
-9	21	3	15.7	8.3
-9	27	3	60.6	56.8
-10	11	3	97.9	98.1
-10	14	3	60.4	96.7
-10	17	3	11.7	10.3
-10	20	3	26.6	23.1
-10	23	3	57.0	65.1
-10	26	3	21.1	31.4
-11	13	3	34.2	28.3
-11	16	3	78.0	81.2
-11	19	3	42.2	52.3
-11	22	3	61.3	64.4
-11	25	3	20.4	18.7
-11	28	3	8.1	16.8
-11	31	3	28.3	33.0
-11	34	3	10.4	12.3
-12	15	3	26.3	37.1
-12	18	3	50.3	38.1
-12	21	3	16.3	10.2
-12	27	3	81.2	52.0
-12	30	3	13.3	9.5
-13	14	3	58.0	62.4
-13	17	3	52.5	55.3
-13	20	3	65.9	68.1
-13	26	3	44.2	49.8
-13	29	3	9.0	12.2
-13	32	3	15.2	19.5
-14	16	3	30.5	30.0
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-14	22	3	61.6	55.8
-14	25	3	15.7	16.4
-14	28	3	52.0	59.4
-15	17	3	25.9	38.1
-15	24	3	27.1	27.1
-15	27	3	23.6	30.3
-15	30	3	12.3	19.2
-16	31	3	39.5	44.3
-16	34	3	6.8	12.7
-16	21	3	60.3	58.7
-16	24	3	25.7	25.5
-16	30	3	31.0	31.3
-16	33	3	15.9	21.2
-17	20	3	35.6	29.4
-17	23	3	9.9	15.2
-17	26	3	8.4	6.7
-17	29	3	18.7	21.1
-18	20	3	28.0	23.5
-18	23	3	11.1	9.9
-18	26	3	9.9	12.3
-18	32	3	13.9	8.8
-19	25	3	15.7	22.2
-19	28	3	6.9	8.6
-19	31	3	12.4	12.8
-20	24	3	7.3	20.5
-20	27	3	22.2	32.3
-20	30	3	13.9	22.2
-21	25	3	27.1	22.8
-21	28	3	15.5	23.3
-21	31	3	7.2	6.2
-22	26	3	26.2	24.6
-22	29	3	6.5	8.1
-23	31	3	12.9	14.9
-23	28	3	15.8	19.3
-23	32	3	20.8	33.6
-24	29	3	6.4	6.8
-24	30	3	8.5	8.1
-24	33	3	12.9	14.9
-25	30	3	10.9	7.2
-25	33	3	7.2	6.2
-26	31	3	21.4	19.6
-26	34	3	9.2	20.4
-27	32	3	11.0	9.3
-28	33	3	10.9	9.2
0	0	4	75.2	84.8
1	0	4	77.3	98.6
2	0	4	143.3	146.1
3	0	4	107.2	105.4
4	0	4	89.3	89.4
5	0	4	17.7	30.5
6	0	4	8.7	2.1
7	0	4	29.9	37.8
8	0	4	146.7	138.5
9	0	4	129.8	110.4
10	0	4	42.5	55.5
11	0	4	40.2	46.0
12	0	4	88.2	105.2
13	0	4	39.5	33.4
14	0	4	6.0	4.3
15	0	4	172.5	161.8
16	0	4	21.8	4.5
17	0	4	118.8	120.8
18	0	4	172.5	161.8
19	0	4	21.8	4.5
20	0	4	118.8	120.8
21	0	4	133.2	112.9
22	0	4	86.2	116.9
23	0	4	101.4	93.3
24	0	4	16.2	10.2
25	0	4	16.4	10.4
26	0	4	44.1	43.9
27	0	4	13.2	14.7
28	0	4	66.0	70.6
29	0	4	110.9	109.9
30	0	4	99.4	100.3
31	0	4	145.9	131.8
32	0	4	13.6	15.9
33	0	4	33.0	33.0
34	0	4	12.6	16.5
35	0	4	15.2	17.0
36	0	4	44.1	42.9
37	0	4	44.1	43.3
38	0	4	86.6	122.5
39	0	4	81.5	78.4
40	0	4	13.0	19.3
41	0	4	55.1	63.0
42	0	4	9.6	15.1
43	0	4	12.9	12.1
44	0	4	51.4	47.7
45	0	4	86.6	79.6
46	0	4	26.7	35.9
47	0	4	230.0	224.0
48	0	4	73.3	80.5
49	0	4	26.4	28.1
50	0	4	65.6	68.7
51	0	4	62.5	69.7
52	0	4	8.2	5.3
53	0	4	13.4	17.8
54	0	4	7.2	10.3
55	0	4	21.2	17.4
56	0	4	54.6	58.8
57	0	4	16.3	18.4
58	0	4	26.1	32.8
59	0	4	58.4	70.8
60	0	4	55.1	42.5
61	0	4	10.6	6.8
62	0	4	21.6	22.7
63	0	4	24.5	23.5
64	0	4	15.7	23.6
65	0	4	23.5	16.7
66	0	4	39.6	24.5
67	0	4	20.9	14.2
68	0	4	23.8	27.6
69	0	4	44.7	51.1
70	0	4	44.3	30.9
71	0	4	8.2	7.2
72	0	4	41.2	41.7
73	0	4	59.7	49.8
74	0	4	39.5	28.6
75	0	4	37.2	36.6
76	0	4	25.9	24.0
77	0	4	110.4	119.9
78	0	4	14.8	4.8
79	0	4	86.9	79.1
80	0	4	68.5	78.0
81	0	4	34.5	32.7
82	0	4	13.7	9.5
83	0	4	15.9	18.7
84	0	4	24.2	25.5
85	0	4	43.4	42.0
86	0	4	17.5	24.6
87	0	4	25.0	21.6
88	0	4	62.4	71.6
89	0	4	24.4	32.5
90	0	4	45.3	44.3
91	0	4	24.0	15.8
92	0	4	51.4	49.5
93	0	4	36.9	24.3
94	0	4	16.7	17.9
95	0	4	25.0	21.6
96	0	4	97.6	95.0
97	0	4	22.3	15.5
98	0	4	8.1	12.5
99	0	4	10.3	13.7
100	0	4	117.3	112.0
101	0	4	96.9	82.1
102	0	4	21.7	23.3
103	0	4	20.7	28.5
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106	0	4	24.1	25.2
107	0	4	25.0	33.3
108	0	4	11.1	5.3
109	0	4	11.7	2.0
110	0	4	20.4	20.3
111	0	4	30.4	39.2
112	0	4	77.0	71.5
113	0	4	20.7	15.7
114	0	4	7.6	15.1
115	0	4	19.3	20.0
116	0	4	41.7	39.5
117	0	4	20.0	18.2
118	0	4	22.2	34.6
119	0	4	17.6	17.4
120	0	4	11.6	8.6
121	0	4	19.2	16.5
122	0	4	9.3	7.8
123	0	4	24.2	26.0
124	0	4	23.7	29.8
125	0	4	23.7	19.9
126	0	4	37.4	36.2
127	0	4	9.4	10.0
128	0	4	8.4	10.0
129	0	4	14.7	14.6
130	0	4	13.7	14.9
131	0	4	14.0	14.0
132	0	4	9.4	3.9
133	0	4	8.1	7.3
134	0	4	37.9	33.7
135	0	4	53.2	55.1
136	0	4	77.3	78.3
137	0	4	45.3	33.1
138	0	4	36.9	48.8
139	0	4	9.9	10.5
140	0	4	12.9	2.4
141	0	4	9.9	10.5
142	0	4	33.6	28.0
143	0	4	75.3	67.0
144	0	4	41.6	43.9
145	0	4	19.7	23.1
146	0	4	10.5	13.6
147	0	4	41.7	23.5
148	0	4	51.9	52.2
149	0	4	70.1	73.9
150	0	4	82.3	86.8
151	0	4	36.0	35.9
152	0	4	37.8	43.7
153	0	4	248.1	233.3
154	0	4	157.9	151.4
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162	0	4	45.4	34.0
163	0	4	26.7	35.9
164	0	4	230.0	224.0
165	0	4	73.3	80.5
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190	0	4	59.7	49.8
191	0	4	39.5	28.6
192	0	4	37.2	36.6
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196	0	4	86.9	79.1
197	0	4	68.5	78.0
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200	0	4	15.9	18.7
201	0	4	24.2	25.5
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238	0	4	19.2	16.5
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246	0	4	14.7	14.6
247	0	4	13.7	14.9
248	0	4	14.0	14.0
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250	0	4	8.1	7.3
251	0	4	37.9	33.7
252	0	4	53.2	55.1
253	0	4	77.3	78.3
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266	0	4	70.1	73.9
267	0	4	82.3	86.8
268	0	4	36.0	35.9
269	0	4	37.8	43.7
270	0	4	248.1	233.3
271	0	4	157.9	151.4
272	0	4	32.6	37.5
273	0	4	51.9	52.2
274	0	4	39.4	28.9
275	0	4	41.7	23.5
276	0	4	12.4	14.7
277	0	4	54.1	46.0
278	0	4	52.8	51.9
279	0	4	45.4	34.0
280	0	4	26.7	35.9
281	0	4	230.0	224.0
282	0	4	73.3	80.5
283	0	4	26.4	28.1
284	0	4	65.6	68.7
285	0	4	62.5	69.7
286	0	4	8.2	5.3
287	0	4	13.4	17.8
288	0	4	7.2	10.3
289	0	4	21.2	17.4
290	0	4	54.6	58.8
291	0	4	16.3	18.4
292	0	4	26.1	32.8
293	0	4	58.4	70.8
294	0	4	55.1	42.5
295	0	4	10.6	6.8
296	0	4	21.6	22.7
297	0	4	24.5	23.5
298	0	4	15.7	23.6
299	0	4	23.5	16.7
300	0	4	39.6	24.5
301	0	4	20.9	14.2
302	0	4	23.8	27.6
303	0	4	44.7	51.1
304	0	4	44.3	30.9
305	0	4	8.2	7.2
306	0	4	41.2	41.7
307	0	4	59.7	49.8
308	0	4	39.5	28.6
309	0	4	37.2	36.6
310	0	4	25.9	24.0
311	0	4	110.4	119.9
312	0	4	14.8	4.8
313	0	4	86.9	79.1
314	0	4	68.5	78.0
315	0	4	34.5	32.7
316	0	4	13.7	9.5
317	0	4	15.9	18.7
318	0	4	24.2	25.5
319	0	4	43.4	42.0
320	0	4	17.5	24.6
321	0	4	25.0	21.6
322	0	4	62.4	71.6
323	0	4	24.4	32.5
324	0	4	45.3	44.3
325	0	4	24.0	15.8
326	0	4	51.4	49.5
327	0	4	36.9	24.3
328	0	4	16.7	17.9
329	0	4	25.0	21.6
330	0	4	97.6	95.0
331	0	4	22.3	15.5
332	0	4	8.1	12.5
333	0	4	10.3	13.7
334	0	4	117.3	112.0
335	0	4	96.9	82.1
336	0	4	21.7	23.3
337	0	4	20.7	28.5
338	0	4	48.7	53.5
339	0	4	19.2	7.6
340	0	4	24.1	25.2
341	0	4	25.0	33.3
342	0	4	11.1	5.3
343	0	4	11.7	2.0
344	0	4	20.4	20.3
345	0	4	30.4	39.2
346	0	4	77.0	71.5
347	0	4	20.7	15.7
348	0	4	7.6	15.1
349	0	4	19.3	20.0
350	0	4	41.7	39.5
351	0	4	20.0	18.2
352	0	4	22.2	34.6
353	0	4	17.6	17.4
354	0	4	11.6	8.6
355	0	4	19.2	16.5
356	0	4	9.3	7.8
357	0	4	24.2	26.0
358	0	4	23.7	29.8
359	0	4	23.7	19.9
360	0	4	37.4	36.2
361	0	4	9.4	10.0
362	0	4	8.4	10.0
363	0	4	14.7	14.6
364	0	4	13.7	14.9
365	0	4	14.0	14.0
366	0	4	9.4	3.9
367	0	4	8.1	7.3
368	0	4	37.9	33.7
369	0	4	53.2	55.1
370	0	4	77.3	78.3
371	0	4	45.3	33.1
372	0	4	36.9	48.8
373	0	4	9.9	10.5
374	0	4	12.9	2.4
375	0	4	9.9	10.5
376	0	4	33.6	28.0
377	0	4	75.3	67.0
378	0	4	41.6	43.9
379	0	4	19.7	23.1
380	0	4	10.5	13.6
381	0	4	41.7	23.5
382	0	4	51.9	52.2
383	0	4	70.1	73.9
384	0	4	82.3	86.8
385	0	4	36.0	35.9
386	0	4	37.8	43.7
387	0	4	248.1	233.3
388	0	4	157.9	151.4
389	0	4	32.6	37.5
390	0	4	51.9

H	K	L	F OBS	F CALC
4	7	6	21x5	13x1
7	7	6	58.7	49.8
14	7	6	29.4	25.8
2	8	6	36.1	32.3
5	8	6	111.0	93.4
11	8	6	49.6	52.6
14	8	6	21.0	23.1
17	8	6	28.4	37.9
20	8	6	18.0	25.9
0	9	6	116.6	111.9
3	9	6	25.0	5.5
9	9	6	30.4	35.3
12	9	6	21.0	19.4
15	9	6	19.9	13.1
21	9	6	7.3	4.8
1	10	6	81.9	82.5
4	10	6	30.7	20.3
10	10	6	18.9	20.3
13	10	6	48.1	53.6
16	10	6	14.8	4.9
2	11	6	27.7	30.7
5	11	6	7.0	11.2
14	11	6	32.7	39.5
20	11	6	17.2	29.6
0	12	6	38.2	24.4
6	12	6	91.9	97.8
9	12	6	39.2	46.6
15	12	6	16.8	16.9
18	12	6	7.0	9.9
1	13	6	18.4	17.0
4	13	6	27.5	30.0
7	13	6	40.4	43.5
10	13	6	19.0	3.9
16	13	6	13.0	8.4
19	13	6	25.4	34.2
2	14	6	41.1	55.0
5	14	6	13.3	11.7
8	14	6	31.9	19.7
11	14	6	11.9	2.8
14	14	6	42.3	39.1
0	15	6	15.9	10.0
3	15	6	20.6	19.1
6	15	6	20.4	4.4
9	15	6	8.0	5.2
12	15	6	20.0	24.6
15	15	6	13.9	10.1
1	16	6	12.2	9.9
4	16	6	15.3	3.2
7	16	6	30.2	26.2
13	16	6	54.2	47.0
1	17	6	53.0	46.3
4	17	6	8.6	17.4
7	17	6	45.1	39.5
13	17	6	12.8	17.7
2	18	6	31.0	21.4
8	18	6	29.4	21.7
11	20	6	9.2	11.9
0	21	6	18.3	15.1
3	21	6	21.5	17.3
6	21	6	15.5	20.5
9	21	6	10.8	12.1
1	22	6	39.3	33.2
7	22	6	21.7	22.1
7	22	6	24.6	23.7
5	23	6	17.8	19.8
8	23	6	34.4	40.9
3	24	6	31.7	21.8
6	24	6	11.4	16.0
1	25	6	24.6	22.6
2	26	6	27.3	15.4
0	27	6	5.3	13.2
-1	2	6	33.3	45.5
-1	5	6	7.5	22.3
-1	8	6	10.2	6.8
-1	11	6	28.9	19.0
-1	14	6	95.9	108.5
-1	17	6	99.7	94.3
-1	20	6	53.5	57.7
-2	6	6	18.6	13.2
-2	4	6	43.2	41.2
-2	7	6	23.3	37.9
-2	10	6	24.3	19.4
-2	13	6	38.2	42.6
-2	16	6	149.7	123.2
-2	19	6	40.4	37.2
-3	5	6	77.4	91.0
-3	9	6	95.2	97.0
-3	12	6	44.1	39.0
-3	15	6	79.8	62.7
-3	18	6	75.8	59.8
-4	21	6	37.4	29.4
-4	5	6	18.3	19.7
-4	8	6	106.3	103.3
-4	11	6	9.9	9.5
-4	14	6	135.4	139.0
-4	20	6	10.2	12.6
-4	23	6	14.8	16.0
-4	26	6	31.3	29.6
-4	27	6	5.0	7.9
-5	7	6	98.7	95.5
-5	13	6	12.2	10.3
-5	16	6	125.6	130.5
-5	19	6	13.3	5.6
-5	22	6	32.9	24.7
-6	7	6	118.5	115.5
-6	12	6	32.2	36.2
-6	15	6	80.2	77.7
-6	21	6	18.2	8.4
-6	24	6	25.4	24.4
-6	27	6	16.4	9.7
-6	30	6	9.0	6.8
-7	8	6	14.5	6.6
-7	11	6	9.9	0.2
-7	14	6	11.3	2.6
-7	17	6	141.9	144.6
-7	23	6	9.4	9.7
-7	29	6	4.9	0.3
-8	10	6	44.0	55.4
-8	13	6	46.1	44.6
-8	16	6	20.2	15.2
-8	19	6	98.9	114.6
-8	22	6	43.3	37.6
-9	25	6	19.8	21.6
-9	28	6	9.9	9.7
-9	15	6	67.6	53.0
-9	18	6	54.7	52.7
H	K	L	F OBS	F CALC
-9	21	6	40.5	43.6
-9	24	6	21.1	19.9
-9	27	6	43.7	41.2
-9	30	6	9.2	7.5
-10	14	6	24.9	8.7
-10	17	6	12.6	25.7
-10	20	6	21.4	16.6
-10	23	6	35.9	44.8
-10	26	6	37.1	43.6
-11	13	6	12.1	27.2
-11	16	6	25.5	29.3
-11	19	6	16.5	30.1
-11	25	6	26.7	30.4
-11	31	6	17.2	14.5
-12	14	6	40.5	44.6
-12	21	6	54.2	53.3
-12	24	6	60.0	69.5
-12	27	6	34.5	30.2
-13	14	6	60.2	66.5
-13	17	6	31.0	21.7
-13	20	6	58.4	51.1
-13	26	6	19.9	11.9
-13	32	6	13.9	17.5
-14	16	6	36.9	30.9
-14	19	6	43.4	41.2
-14	25	6	35.6	38.6
-14	28	6	11.3	13.7
-14	31	6	19.9	23.5
-15	18	6	49.4	40.0
-15	24	6	22.3	21.1
-15	30	6	12.4	4.6
-16	17	6	13.2	3.6
-16	20	6	21.0	12.5
-16	26	6	22.4	21.2
-16	29	6	11.8	11.0
-17	19	6	10.2	5.0
-17	28	6	9.4	16.5
-17	31	6	9.3	11.7
-18	21	6	16.1	18.7
-18	24	6	9.8	2.0
-18	27	6	12.4	8.8
-19	23	6	13.4	7.9
-19	26	6	15.0	8.5
-19	32	6	13.5	13.0
-20	25	6	19.2	10.0
-20	25	6	28.9	17.1
-20	31	6	10.5	5.9
-21	24	6	10.6	12.2
-21	27	6	26.8	36.4
-21	30	6	10.2	9.9
-22	23	6	67.2	57.5
-22	26	6	18.0	15.9
-23	25	6	19.3	33.7
-23	31	6	11.6	8.3
-24	27	6	13.6	14.3
-23	31	6	11.6	8.3
-24	27	6	10.6	12.2
-25	26	6	26.8	36.4
-25	29	6	12.3	10.8
1	0	7	30.4	48.3
1	3	7	43.7	12.9
1	6	7	61.8	52.0
1	9	7	93.0	55.7
1	12	7	33.5	39.3
1	15	7	22.5	26.2
1	18	7	19.3	17.5
1	21	7	21.5	19.4
1	24	7	42.7	41.6
1	27	7	24.1	13.5
1	30	7	5b.9	54.2
2	1	7	29.9	15.5
2	4	7	26.6	24.6
2	7	7	16.5	18.6
2	10	7	99.5	136.7
2	13	7	34.4	40.0
2	16	7	13.2	12.7
2	19	7	90.3	79.3
2	22	7	46.6	38.1
2	25	7	29.4	24.5
3	0	7	29.8	33.9
3	3	7	104.1	114.8
3	6	7	77.0	73.2
3	9	7	40.2	34.6
3	12	7	94.8	73.7
3	15	7	10.9	9.1
3	18	7	45.6	45.5
3	21	7	35.8	36.0
3	24	7	20.7	25.2
3	27	7	19.9	36.6
4	1	7	27.5	27.5
4	4	7	23.1	24.3
4	7	7	23.9	14.2
4	10	7	25.0	24.6
4	13	7	63.4	63.4
4	16	7	77.4	73.4
4	19	7	14.7	19.2
4	22	7	12.7	14.2
4	25	7	30.0	30.0
4	28	7	52.6	38.0
5	2	7	50.0	39.1
5	5	7	30.8	29.3
5	8	7	40.3	36.4
5	11	7	73.7	84.8
5	14	7	36.5	34.6
5	17	7	76.6	80.9
5	20	7	37.0	45.2
5	23	7	14.8	22.9
5	26	7	32.3	18.5
5	29	7	31.7	33.9
6	0	7	29.0	32.0
6	3	7	103.2	93.3
6	6	7	78.5	75.4
6	9	7	53.6	45.8
6	12	7	43.9	23.1
6	15	7	23.4	21.9
6	18	7	33.9	35.0
6	21	7	21.2	18.9
6	24	7	13.4	7.9
6	27	7	39.5	26.7
6	30	7	17.0	24.5
7	1	7	26.0	26.6
7	4	7	28.9	22.8
7	7	7	13.7	18.7
7	10	7	41.4	41.6
7	13	7	33.2	30.5
7	16	7	146.5	143.9
7	19	7	25.3	19.4
7	22	7	55.4	43.1
7	25	7	12.0	10.9
7	28	7	39.4	39.6
8	2	7	40.3	38.4
8	5	7	33.9	35.4
8	8	7	21.2	18.9
8	11	7	10.3	35.0
8	14	7	12.3	10.4
8	17	7	39.5	26.7
8	20	7	24.4	22.4
8	23	7	19.4	17.9
8	26	7	12.5	10.7
8	29	7	40.3	38.9
9	1	7	33.9	36.4
9	4	7	33.7	30.4
H	K	L	F OBS	F CALC
-10	22	7	28.2	27.6
-19	25	7	31.7	26.1
-20	21	7	22.5	20.5
-20	30	7	12.3	10.5
-21	23	7	23.4	10.9
-21	29	7	9.6	13.3
-22	28	7	9.2	11.3
-23	24	7	17.9	13.9
-26	27	7	14.3	20.9
2	0	8	15.0	7.5
5	0	8	34.1	31.5
8	0	8	46.1	69.8
11	0	8	16.5	4.3
14	0	8	28.8	14.8
17	0	8	29.4	28.0
20	0	8	26.1	22.6
0	1	8	27.5	52.9
3	1	8	15.0	7.5
6	1	8	68.9	65.0
9	1	8	14.2	15.7
12	1	8	100.6	100.7
15	1	8	36.2	35.9
18	1	8	20.6	10.5
21	1	8	21.6	21.3
24	1	8	43.4	41.2
1	2	8	45.3	121.4
4	2	8	11.0	0.9
7	2	8	25.7	27.1
10	2	8	13.0	3.3
13	2	8	42.7	35.9
16	2	8	43.4	38.0
2	3	8	32.3	34.1
5	3	8	52.2	49.6
8	3	8	39.2	45.8
11	3	8	11.5	8.6
14	3	8	10.0	3.0
23	3	8	17.7	12.6
0	4	8	9.9	9.2
3	4	8	68.6	75.0
6	4	8	39.9	42.8
9	4	8	31.7	32.9
12	4	8	41.7	31.8
15	4	8	40.5	40.7
18	4	8	44.7	33.3
21	4	8	21.7	9.6
24	4	8	24.9	29.5
1	5	8	56.2	61.3
4	5	8	53.3	50.2
7	5	8	43.8	39.4
10	5	8	24.7	29.2
13	5	8	39.2	36.3
16	5	8	40.6	32.4
19	5	8	22.3	19.2
22	5	8	22.3	19.2
1	6	8	21.1	20.4
4	6	8	24.9	29.5
7	6	8	56.2	39.3
10	6	8	18.2	15.2
13	6	8	15.2	19.1
16	6	8	38.6	27.5
19	6	8	55.5	51.1
22	6	8	21.1	8.3
25	6	8	24.9	24.5
28	6	8	74.0	71.0
31	6	8	32.8	31.7
34	6	8	27.4	21.5
37	6	8	12.5	7.8
40	6	8	102.9	90.9
43	6	8	29.3	32.2
46	6	8	23.9	11.6
49	6	8	34.4	24.0
52	6	8	23.3	14.0
55	6	8	45.1	39.2
58	6	8	25.4	17.2
61	6	8	39.3	41.4
64	6	8	33.7	25.9
67	6	8	15.9	11.6
70	6	8	28.0	26.7
73	6	8	25.1	10.3
76	6	8	35.3	27.2
79	6	8	44.4	38.4
82	6	8	9.0	9.8
85	6	8	37.5	36.4
88	6	8	14.9	19.3
91	6	8	18.2	29.9
94	6	8	7.6	6.5
97	6	8	15.6	11.6
100	6	8	15.6	18.0
103	6	8	23.3	21.8
106	6	8	13.5	19.6
109	6	8	22.7	20.5
112	6	8	8.1	3.3
115	6	8	17.3	18.4
118	6	8	24.5	21.2
121	6	8	8.1	3.3
124	6	8	62.8	55.4
127	6	8	16.4	17.4
130	6	8	10.1	14.5
133	6	8	12.3	7.7
136	6	8	29.2	32.5
139	6	8	57.4	58.3
142	6	8	14.0	3.6
145	6	8	44.2	39.7
148	6	8	10.4	9.1
151	6	8	13.4	16.9
154	6	8	17.4	14.5
157	6	8	18.4	19.7
160	6	8	25.5	18.7
163	6	8	17.4	14.5
166	6	8	18.4	19.7
169	6	8	25.5	18.7
172	6	8	13.4	7.4
175	6	8	31.4	32.5
178	6	8	13.4	7.4
181	6	8	31.4	27.6
184	6	8	12.4	10.6
187	6	8	18.4	18.0
190	6	8	13.4	7.4
193	6	8	31.4	27.6
196	6	8	12.4	10.6
199	6	8	18.4	18.0
202	6	8	13.4	7.4
205	6	8	31.4	27.6
208	6	8	12.4	10.6
211	6	8	18.4	18.0
214	6	8	13.4	7.4
217	6	8	31.4	27.6
220	6	8	12.4	10.6
223	6	8	18.4	18.0
226	6	8	13.4	7.4
229	6	8	31.4	27.6
232	6	8	12.4	10.6
235	6	8	18.4	18.0
238	6	8	13.4	7.4
241	6	8	31.4	27.6
244	6	8	12.4	10.6
247	6	8	18.4	18.0
250	6	8	13.4	7.4
253	6	8	31.4	27.6
256	6	8	12.4	10.6
259	6	8	18.4	18.0
262	6	8	13.4	7.4
265	6	8	31.4	27.6
268	6	8	12.4	10.6
271	6	8	18.4	18.0
274	6	8	13.4	7.4
277	6	8	31.4	27.6
280	6	8	12.4	10.6
283	6	8	18.4	18.0
286	6	8	13.4	7.4
289	6	8	31.4	27.6
292	6	8	12.4	10.6
295	6	8	18.4	18.0
298	6	8	13.4	7.4
301	6	8	31.4	27.6
304	6	8	12.4	10.6
307	6	8	18.4	18.0
310	6	8	13.4	7.4
313	6	8	31.4	27.6
316	6	8	12.4	10.6
319	6	8	18.4	18.0
322	6	8	13.4	7.4
325	6	8	31.4	27.6
328	6	8	12.4	10.6
331	6	8	18.4	18.0
334	6	8	13.4	7.4
337	6	8	31.4	27.6
340	6	8	12.4	10.6
343	6	8	18.4	18.0
346	6	8	13.4	7.4
349	6	8	31.4	27.6
352	6	8	12.4	10.6
355	6	8	18.4	18.0
358	6	8	13.4	7.4
361	6	8	31.4	27.6
364	6	8	12.4	10.6
367	6	8	18.4	18.0
370	6	8	13.4	7.4
373	6	8	31.4	27.6
376	6	8	12.4	10.6
379	6	8	18.4	18.0
382	6	8	13.4	7.4
385	6	8	31.4	27.6
388	6	8	12.4	10.6
391	6	8	18.4	18.0
394	6	8	13.4	7.4
397	6	8	31.4	27.6
400	6	8	12.4	10.6
403	6	8	18.4	18.0
406	6	8	13.4	7.4
409	6	8	31.4	27.6
412	6	8	12.4	10.6
415	6	8	18.4	18.0
418	6	8	13.4	7.4
421	6	8	31.4	27.6
424	6	8	12.4	10.6
427	6	8	18.4	18.0
430	6	8	13.4	7.4
433	6	8	31.4	27.6
436	6	8	12.4	10.6
439	6	8	18.4	18.0
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445	6	8	31.4	27.6
448	6	8	12.4	10.6
451	6	8	18.4	18.0
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457	6	8	31.4	27.6
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472	6	8	12.4	10.6
475	6	8	18.4	18.0
478	6	8	13.4	7.4
481	6	8	31.4	27.6
484	6	8	12.4	10.6
487	6	8	18.4	18.0
490	6	8	13.4	7.4
493	6	8	31.4	27.6
496	6	8	12.4	10.6
499	6	8	18.4	18.0
502	6	8	13.4	7.4
505	6	8	31.4	27.6
508	6	8	12.4	10.6
511	6	8	18.4	18.0
514	6	8	13.4	7.4
517	6	8	31.4	27.6
520	6	8	12.4	10.6
523	6	8	18.4	18.0
526	6	8	13.4	7.4
529	6	8	31.4	27.6
532	6	8	12.4	10.6
535	6	8	18.4	18.0
538	6	8	13.4	7.4
541	6	8	31.4	27.6
544	6	8	12.4	10.6
547	6	8	18.4	18.0
550	6	8	13.4	7.4
553	6	8	31.4	27.6
556	6	8	12.4	10.6
559	6	8	18.4	18.0
562	6	8	13.4	7.4
565	6	8	31.4	27.6
568	6	8	12.4	10.6
571	6	8	18.4	18.0
574	6	8	13.4	7.4
577	6	8	31.4	27.6
580	6	8	12.4	10.6
583	6	8	18.4	18.0
586	6	8	13.4	7.4
589	6	8	31.4	27.6
592	6	8	12.4	10.6
595	6	8	18.4	18.0
598	6	8	13.4	7.4
601	6	8	31.4	27.6
604	6	8	12.4	10.6
607	6	8	18.4	18.0
610	6	8	13.4	7.4
613	6	8	31.4	27.6
616	6	8	12.4	10.6
619	6	8	18.4	18.0
622	6	8	13.4	7.4
625	6	8	31.4	27.6
628	6	8	12.4	10.6
631	6	8	18.4	18.0
634	6	8	13.4	7.4
637	6	8	31.4	27.6
640	6	8	12.4	10.6
643	6	8	18.4	18.0
646	6	8	13.4	7.4
649	6	8	31.4	27.6
652	6	8	12.4	10.6
655	6	8	18.4	18.0
658	6	8	13.4	7.4
661	6	8	31.4	27.6
664	6	8	12.4	10.6
667	6	8	18.4	18.0
670	6	8	13.4	7.4
673	6	8	31.4	27.6
676	6	8	12.4	10.6
679	6	8	18.4	18.0
682	6	8	13.4	7.4
685	6	8	31.4	27.6
688	6	8	12.4	10.6
691	6	8	18.4	18.0
694	6	8	13.4	7.4
697	6	8	31.4	27.6
700	6	8	12.4	10.6
703	6	8	18.4	18.0
706	6	8	13.4	7.4
709	6	8	31.4	27.6
712	6	8	12.4	10.6
715	6	8	18.4	18.0
718	6	8	13.4	7.4
721	6	8	31.4	27.6
724	6	8	12.4	10.6
727	6	8	18.4	18.0
730	6	8	13.4	7.4
733	6	8	31.4	27.6
736	6	8	12.4	10.6
739	6	8	18.4	18.0
742	6	8	13.4	7.4
745	6	8	31.4	27.6
748	6	8	12.4	10.6
751	6	8	18.4	18.0
754	6	8	13.4	7.4
757	6	8	31.4	27.6
760	6	8	12.4	10.6
763	6	8	18.4	18.0
766	6	8	13.4	7.4
769	6	8	31.4	27.6
772	6	8	12.4	10.6
775	6	8	18.4	18.0
778	6	8	13.4	7.4
781	6	8	31.4	27.6
784	6	8	12.4	10.6
787	6	8	18.4	18.0
790	6	8	13.4	7.4
793	6	8	31.4	27.6
796	6	8	12.4	10.6
799	6	8	18.4	18.0
802	6	8	13.4	7.4
805	6	8	31.4	27.6
808	6	8	12.4	10.6
811	6	8	18.4	18.0
814	6	8	13.4	7.4
817	6	8	31.4	27.6
820	6	8	12.4	10.6
823	6	8	18.4	18.0
826	6	8	13.4	7.4
829	6	8	31.4	27.6
832	6	8	12.4	10.6
835	6	8	18.4	18.0
838	6	8	13.4	7.4
841	6	8	31.4	27.6
844	6	8	12.4	10.6
847	6	8	18.4	18.0
850	6	8	13.4	7.4
853	6	8	31.4	27.6
856	6	8	12.4	10.6
859	6	8	18.4	18.0
862	6	8	13.4	7.4
865	6	8	31.4	27.6
868	6	8

TABLE 2.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X'	Y'	Z
S(1)	6.379 ± 2	-1.531 ± 2	7.120 ± 2
C(2)	5.408 ± 6	-0.139 ± 6	6.495 ± 6
C(3)	6.308 ± 6	0.757 ± 6	5.652 ± 6
C(4)	6.936 ± 5	0.180 ± 5	4.374 ± 6
C(5)	8.528 ± 7	-1.637 ± 8	3.691 ± 7
C(6)	9.180 ± 7	-2.860 ± 9	3.835 ± 9
C(7)	8.936 ± 7	-3.629 ± 8	4.957 ± 9
C(8)	8.054 ± 7	-3.175 ± 6	5.889 ± 8
C(9)	7.396 ± 5	-1.959 ± 6	5.762 ± 7
C(10)	7.621 ± 5	-1.155 ± 6	4.621 ± 6
C(11)	5.891 ± 5	0.078 ± 5	3.248 ± 6
C(12)	5.209 ± 6	1.206 ± 6	2.814 ± 7
C(13)	4.256 ± 6	1.171 ± 6	1.817 ± 7
C(14)	3.959 ± 5	-0.030 ± 6	1.194 ± 6
C(15)	4.615 ± 6	-1.173 ± 6	1.581 ± 6
C(16)	5.570 ± 6	-1.120 ± 5	2.597 ± 6
C(17)	7.990 ± 7	1.220 ± 7	3.940 ± 7
C(18)	4.999 ± 8	0.642 ± 8	7.752 ± 8
C(19)	4.158 ± 6	-0.637 ± 7	5.785 ± 7
O(20)	3.002 ± 5	-0.118 ± 5	0.216 ± 5

C(21)	0.527 ± 18	1.309 ± 15	2.912 ± 16
C(22)	0.000 ± 0	0.000 ± 0	3.435 ± 15
C(23)	0.000 ± 0	0.000 ± 0	4.862 ± 18

TABLE 2.6

HOST BOND LENGTHS AND E.S.D.S.

S(1) - C(2)	1.809 ± 6 Å	C(6) - C(7)	1.382 ± 12 Å
S(1) - C(9)	1.749 ± 6	C(7) - C(8)	1.360 ± 11
C(2) - C(3)	1.524 ± 8	C(8) - C(9)	1.389 ± 9
C(2) - C(18)	1.535 ± 10	C(9) - C(10)	1.413 ± 9
C(2) - C(19)	1.522 ± 9	C(11)- C(12)	1.388 ± 8
C(3) - C(4)	1.536 ± 8	C(11)- C(16)	1.400 ± 8
C(4) - C(10)	1.521 ± 8	C(12)- C(13)	1.380 ± 9
C(4) - C(11)	1.540 ± 8	C(13)- C(14)	1.385 ± 8
C(4) - C(17)	1.543 ± 9	C(14)- C(15)	1.373 ± 8
C(5) - C(6)	1.393 ± 11	C(14)- O(20)	1.371 ± 7
C(5) - C(10)	1.386 ± 9	C(15)- C(16)	1.396 ± 8

TABLE 2.7

HOST INTERBOND ANGLES AND E.S.D.S.

C(2) - S(1) - C(9)	103.4 ± 3°	C(7) - C(8) - C(9)	122.4 ± 7°
S(1) - C(2) - C(3)	109.1 ± 4	S(1) - C(9) - C(8)	114.8 ± 5
S(1) - C(2) - C(18)	104.6 ± 5	S(1) - C(9) - C(10)	125.4 ± 4
S(1) - C(2) - C(19)	110.5 ± 4	C(8) - C(9) - C(10)	119.8 ± 6
C(3) - C(2) - C(18)	108.1 ± 5	C(4) - C(10)- C(5)	119.4 ± 6
C(3) - C(2) - C(19)	114.8 ± 5	C(4) - C(10)- C(9)	124.0 ± 5
C(18)- C(2) - C(19)	109.3 ± 5	C(5) - C(10)- C(9)	116.6 ± 6
C(2) - C(3) - C(4)	118.7 ± 5	C(4) - C(11)- C(12)	120.5 ± 5
C(3) - C(4) - C(10)	112.2 ± 5	C(4) - C(11)- C(16)	123.5 ± 5
C(3) - C(4) - C(11)	110.9 ± 4	C(12)- C(11)- C(16)	116.0 ± 5
C(3) - C(4) - C(17)	105.1 ± 5	C(11)- C(12)- C(13)	123.0 ± 5
C(10)- C(4) - C(11)	111.5 ± 4	C(12)- C(13)- C(14)	119.7 ± 5
C(10)- C(4) - C(17)	109.3 ± 5	C(13)- C(14)- C(15)	119.5 ± 5
C(11)- C(4) - C(17)	107.6 ± 5	C(13)- C(14)- O(20)	121.7 ± 5
C(6) - C(5) - C(10)	122.9 ± 7	C(15)- C(14)- O(20)	118.8 ± 5
C(5) - C(6) - C(7)	119.3 ± 7	C(14)- C(15)- C(16)	120.0 ± 5
C(6) - C(7) - C(8)	119.1 ± 7	C(11)- C(16)- C(15)	121.9 ± 5

TABLE 2.8

HOST - HOST INTERMOLECULAR CONTACTS BELOW 4 Å

O(20)....O(20)	i	3.04 Å	C(8).....C(6)	v	3.84 Å
C(13)....O(20)	iii	3.61	C(16)....C(17)	vi	3.85
C(15)....C(18)	ii	3.63	C(7).....C(6)	v	3.85
C(7).....C(16)	v	3.72	C(7).....C(15)	v	3.87
C(5).....C(12)	vi	3.73	C(16)....C(18)	ii	3.88
C(6).....C(13)	vi	3.74	C(8).....C(7)	v	3.90
C(14)....O(20)	iii	3.76	C(6).....C(15)	v	3.92
S(1).....C(12)	ii	3.77	C(14)....O(20)	i	3.93
C(17)....C(7)	iv	3.82	C(15)....O(20)	i	3.97
C(6).....C(12)	vi	3.83	C(15)....C(17)	vi	3.97
C(5).....C(13)	vi	3.84	S(1).....C(3)	vii	3.98

Roman numerals refer to the transformations of the fractional coordinates given in Table 2.2.

i	y,	y - x,	-z;	v	$\frac{2}{3}$ + y - x, $\frac{1}{3}$ - x, $\frac{1}{3}$ + z;
ii	y,	y - x,	1 - z;	vi	$\frac{2}{3}$ - x, $\frac{1}{3}$ - y, $\frac{1}{3}$ - z;
iii	x - y,	x,	-z;	vii	$\frac{2}{3}$ - x, $\frac{1}{3}$ - y, $1\frac{1}{3}$ - z;
iv	$\frac{1}{3}$ + y,	$\frac{2}{3}$ + y - x,	$\frac{2}{3}$ - z;		

The transformations are applied to the coordinates of the second atom in each case.

TABLE 2.9

GUEST BOND LENGTHS AND E.S.D.S.

C(21)- C(22)	1.505 ± 16 Å	C(23)- C(24)	1.262 ± 26 Å
C(22)- C(23)	1.427 ± 24		

TABLE 2.10

GUEST INTERBOND ANGLES AND E.S.D.S.

C(21)- C(22)- C(23)	110.3 ± 8°	C(22)- C(23)- C(24)	180.0 ± 0
C(21)- C(22)- C(27)	108.6 ± 9		

TABLE 2.11

HOST - GUEST INTERMOLECULAR CONTACTS BELOW 4 Å

C(21)....O(20)	ii	3.53 Å	C(21)....C(19)	iii	3.68 Å
C(21)....O(20)	i	3.58	C(21)....C(14)	i	3.70
C(21)....C(18)	iii	3.64	C(21)....C(15)	i	3.98

Roman numerals refer to the transformations of the fractional coordinates given in Table 2.2.

i -y, x - y, z; iii x - y, x, 1 - z;

ii x - y, x, -z;

The transformations are applied to the coordinates of the second atom in each case.

2.3 Discussion

Previous analyses (Chapter 1), Flippen et al., (1970) leads to the conclusion that detailed structural information related to the guest molecule will only be obtained "directly" when the following requirements are met:

(i) the molecular symmetry of the guest molecule(s) must be compatible with the symmetry of the cavity, viz., C_{3i} ($\bar{3}$);

(ii) the van der Waals' model of the guest molecule must conform to the approximate shape and volume of the empty cavity.

If criterion (i) is not satisfied the guest molecule will be disordered within the cavity and if (ii) is not satisfied the subsequent motion of the guest molecule within the cavity may render it unresolvable by X-ray methods at room temperature.

The acetylenic guest, 2,5,5-trimethylhex-3-yn-2-ol, was considered a suitable choice for inclusion and investigation on the basis of its molecular shape and volume. This has been justified by the success of the subsequent analysis, which represents the first unambiguous determination of the orientation, conformation and dimensions of a guest molecule within the cavity of an organic clathrate (MacNicol and Wilson, 1971).

Within the cavity, as can be seenfrom Fig. 2.2, the guest

molecule (II) is co-linear with the c-axis, the acetylenic unit fitting neatly into the waist of the cavity, leaving a tetrahedral unit in each half. Since the molecules comprising the walls of the cage are related by $\bar{3}$ symmetry, this imposes on the contents of the cavity $\bar{3}$ symmetry. However the disorder inherent in the tetrahedral unit may be neglected if a weighted average of the hydroxy and methyl groups is assumed. It is possible, on this basis, to distinguish between the staggered and eclipsed conformations of (II) since only the former would give rise to an electron density distribution as shown in Fig. 2.3.

The conformation of (II) within the cavity is staggered, a conformation imposed on it by the van der Waals' surface of the cavity. Thus the interaction between the tetrahedral unit of the guest molecule and the host molecules, as shown in Fig. 2.4, is such as to attenuate the librational motion of the guest molecule within the cavity at room temperature. This may be taken as an illustration of a "lock and key" type interaction in which the conformation of the guest molecule is governed by the host.

Although the orientation and conformation of the guest molecule within the cavity and the molecular dimensions of the co-linear unit within the cavity (C≡C : 1.26 Å; C-C≡C : 1.43 Å) have been determined, the statistical disorder present does not allow the accurate dimensions of the tetrahedral unit within the

cavity to be determined. However a weighted average based on the assumed bond lengths, C-C : 1.54 Å; C-O : 1.43 Å, gives 1.52 Å which is concordant with the experimental value of 1.51 Å.

Chapter 3

The Crystal and Molecular Structure of 4-*p*-Hydroxyphenyl-2,2,4-trimethylchroman

3.1 Experimental

Crystal Data

Host: 4-p-hydroxyphenyl-2,2,4-trimethylchroman

Guest: -

$C_{18}H_{20}O_2$ F.W. = 268.4

Trigonal, a = 26.94 Å, c = 10.94 Å, (referred to hexagonal axes)

U = 6872 $Å^3$ F(000) = 2592 electrons

D_m = 1.16 $g.cm.^{-3}$ Z = 18 D_x = 1.167 $g.cm.^{-3}$

Space group: $R\bar{3}$ (C_{3i}^2, No. 148)

Linear absorption coefficient (Cu K_α, λ = 1.5418 Å) = 6 $cm.^{-1}$

The crystals used in this analysis were supplied by Dr. D.D. MacNicol. They consisted of colourless hexagonal needles elongated along the c-axis. Unit cell dimensions were obtained from rotation and Weissenberg photographs (Cu K_α radiation, λ = 1.5418 Å) taken about the c-axis. Since the crystals are isomorphous with the ethanol included clathrate of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman, the space group is $R\bar{3}$ (No. 148)

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the hki0,...hki9 reciprocal lattice nets taken with Cu K_α radiation. The multiple film technique of Robertson, (1943) was used. The observed intensities were reduced to structure amplitudes by applying the

appropriate Lorentz, polarisation and rotation factors (Tunell, 1939). 2630 independent structure amplitudes (Table 3.4) were obtained which represents 75 % of the data accessible to Cu K_α radiation. No absorption corrections were applied.

The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

3.2 Solution and Refinement of the Structure

The unit cell parameters and space group symmetry of 4-p-hydroxyphenyl-2,2,4-trimethylchroman (Dianin's compound) lead to the conclusion that the structure is isomorphous with the ethanol included clathrate of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman.

The coordinates of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman from a previous analysis (Table 1.2) were used in conjunction with the observed structure amplitudes to phase an electron density synthesis from which the coordinates of the atoms of 4-p-hydroxyphenyl-2,2,4-trimethylchroman were obtained. The R-factor was reduced from an initial value of 0.48 to 0.207 in five successive cycles of Fourier refinement.

The structure was further refined in eight cycles of least-squares minimisation of the function $M = \Sigma w(|F_o| - |F_c|)^2$. D.R. Pollard's least-squares program, (1968) was used in the initial stages of the refinement. Each reciprocal lattice net was given an individual scale factor and each atom an individual isotropic temperature factor. The observations were all given unit weight. After three cycles of full matrix least-squares refinement, the R-factor was reduced to 0.157.

A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_3|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 2/|F_o|_{max}$, which has been recommended by Cruickshank, (1961) for use with photographic data, was then applied and a further cycle of least-squares refinement calculated. The residual was reduced to 0.154.

The Glasgow S.F.L.S. program (Cruickshank and Smith, 1965) was then used to continue the refinement. Since the observations were collected up only one axis, there was insufficient information to refine both anisotropic temperature factors and individual layer scale factors. Thus individual anisotropic thermal parameters and a single overall scale factor were refined. As a result of allowing for the anisotropic vibrations of the atoms, a further four cycles of least-squares refinement in which the block diagonal approximation to the normal matrix was applied, reduced the R-factor to 0.118. The weighting scheme applied in the last four cycles of refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$$

where $p_1 = 10$, $p_2 = 0.05$ and $p_3 = 0.002$. No shifts greater than 0.2σ in atomic coordinates or thermal parameters were observed in the final cycle of refinement. The course of the refinement is summarised in Table 3.1.

The structure factors calculated in the final cycle of least-squares refinement were used to calculate a difference synthesis of the cavity. No peaks, apart from random fluctuations of electron

density, were present, indicating the absence of included molecules from the cavity.

Tables 3.2 and 3.3 contain the final values of the fractional atomic coordinates and anisotropic temperature factors together with their standard deviations. The observed and final calculated structure amplitudes are given in Table 3.4. Atomic coordinates in Angstroms referred to orthogonal axes defined by X' parallel to $\underline{a}^*$, Y' normal to $\underline{a}^*$ and $\underline{c}$ and Z parallel to $\underline{c}$ are given in Table 3.5. Tables 3.6 and 3.7 contain the bond lengths and interbond angles in the structure together with their estimated standard deviations. Table 3.8 lists all intermolecular contacts between the atoms which are less than 4 Å. In Table 3.9 the equations of the mean molecular planes through portions of the molecule are given, together with the deviations of certain atoms from these planes. Estimated standard deviations, where quoted, are in units of the last decimal place of the quantity to which they refer.

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 3.1. The chroman residue projected along a line in the mean plane through O(1), C(4), C(9) and C(10) is shown in Fig. 3.2. The general packing of the molecules in the unit cell, as projected on (001) is illustrated in Fig. 3.3. In Figs. 3.4 and 3.5 the structure is shown as viewed along the normal to the $\underline{a}$ and $\underline{c}$ axes, illustrating the cavity.

In Fig. 3.5 two molecules of the host which lie directly above and below the cavity, as viewed in this direction, have been excluded apart from their hydroxyl oxygen atoms. A section through the van der Waals' surface of the cavity is shown in Fig. 3.6.

TABLES AND DIAGRAMS

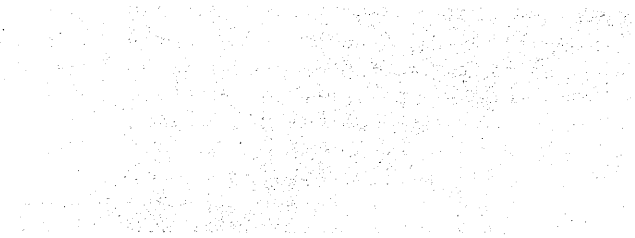
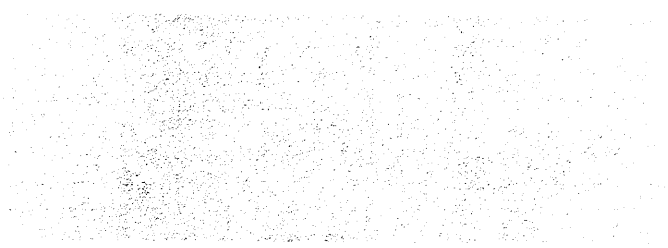


FIGURE 3.1

A molecular drawing illustrating the numbering of the non-hydrogen atoms of the host.



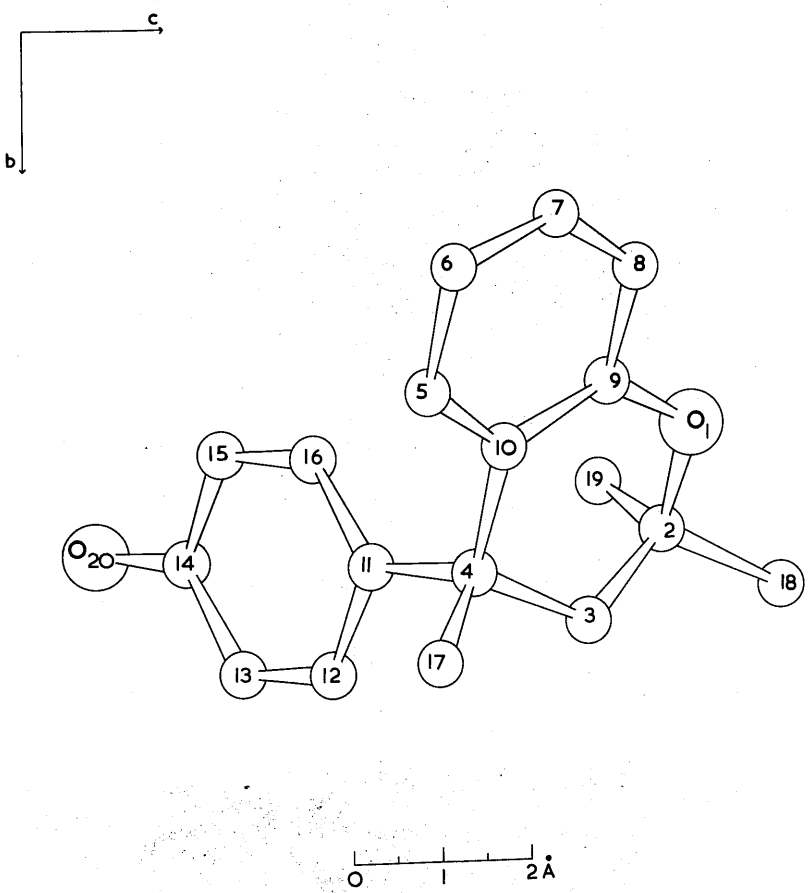

c
b
7
6
8
5
9
O1
10
15
16
19
2
O20
14
11
4
18
3
17
13
12
0
1
2 Å

FIGURE 3.2

A molecular drawing illustrating the chroman residue projected along a line in the mean molecular plane through O(1), C(4), C(9) and C(10).

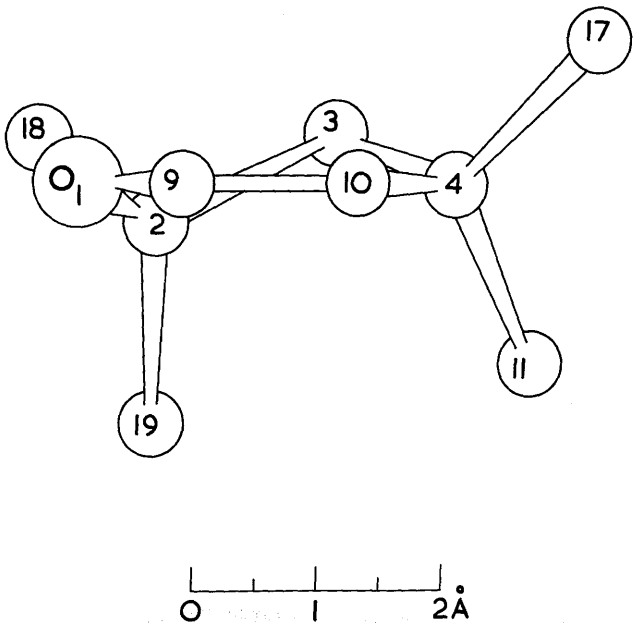

17
18
3
O1
9
10
4
2
11
19
0
1
2Å

FIGURE 3.3

The molecular packing viewed down the c-axis.

b
a
1/3
1/6
1/3
1/6
1/3
1/6
1/3
1/6

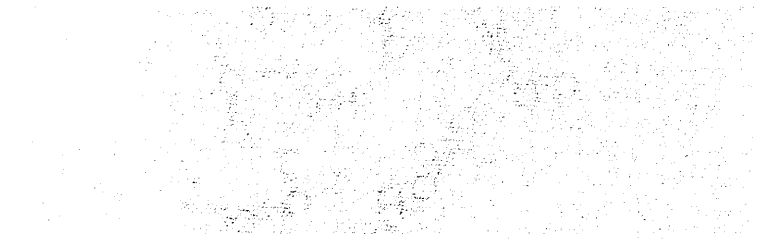
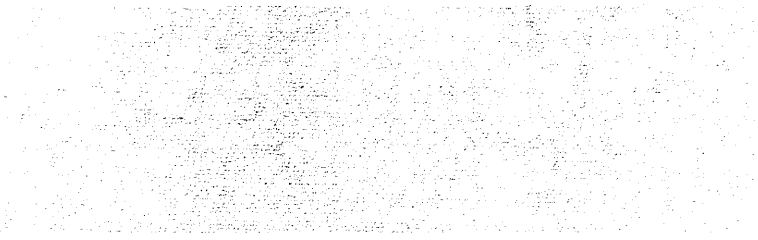


FIGURE 3.4

The packing of the molecules as projected on (010).



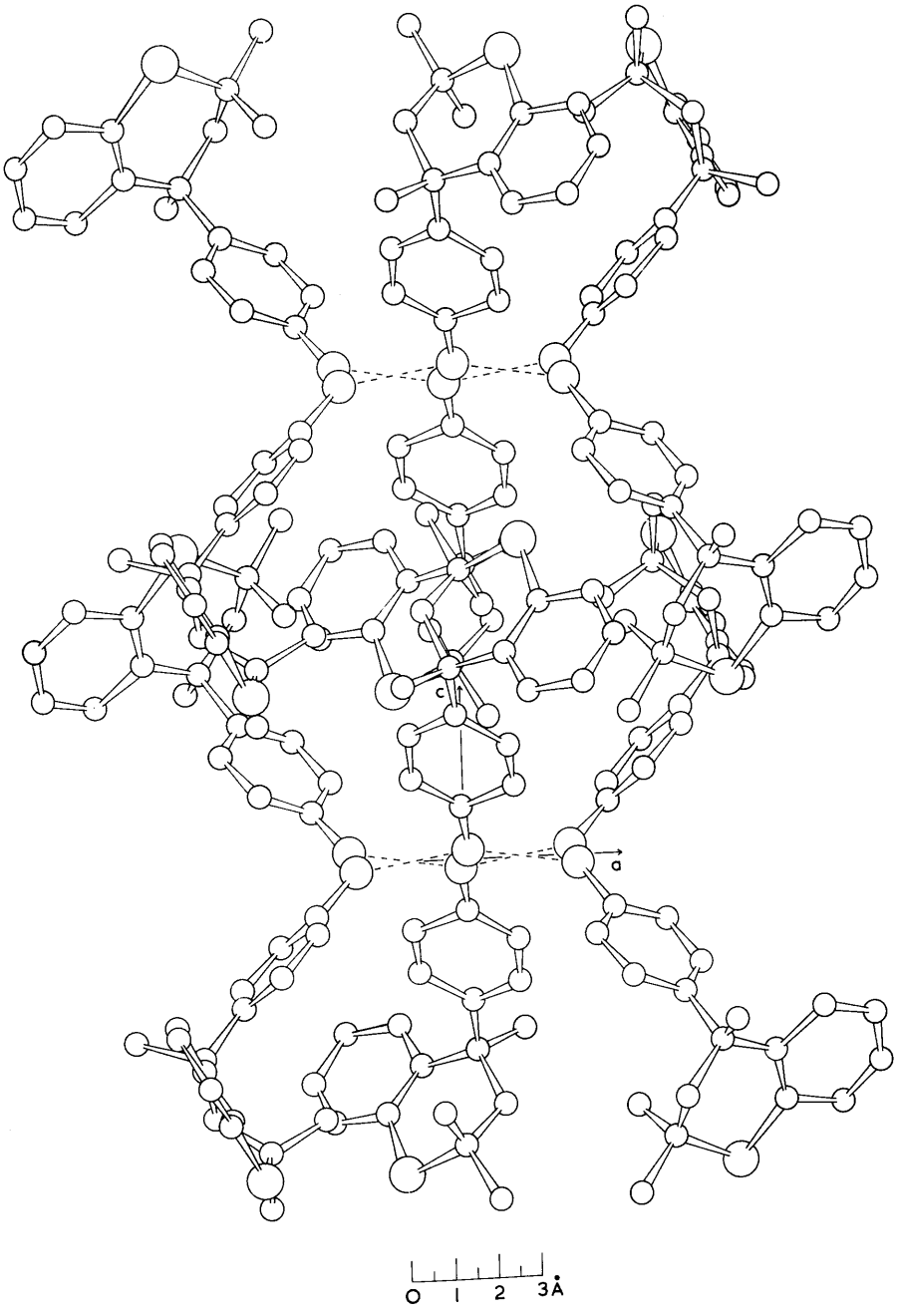
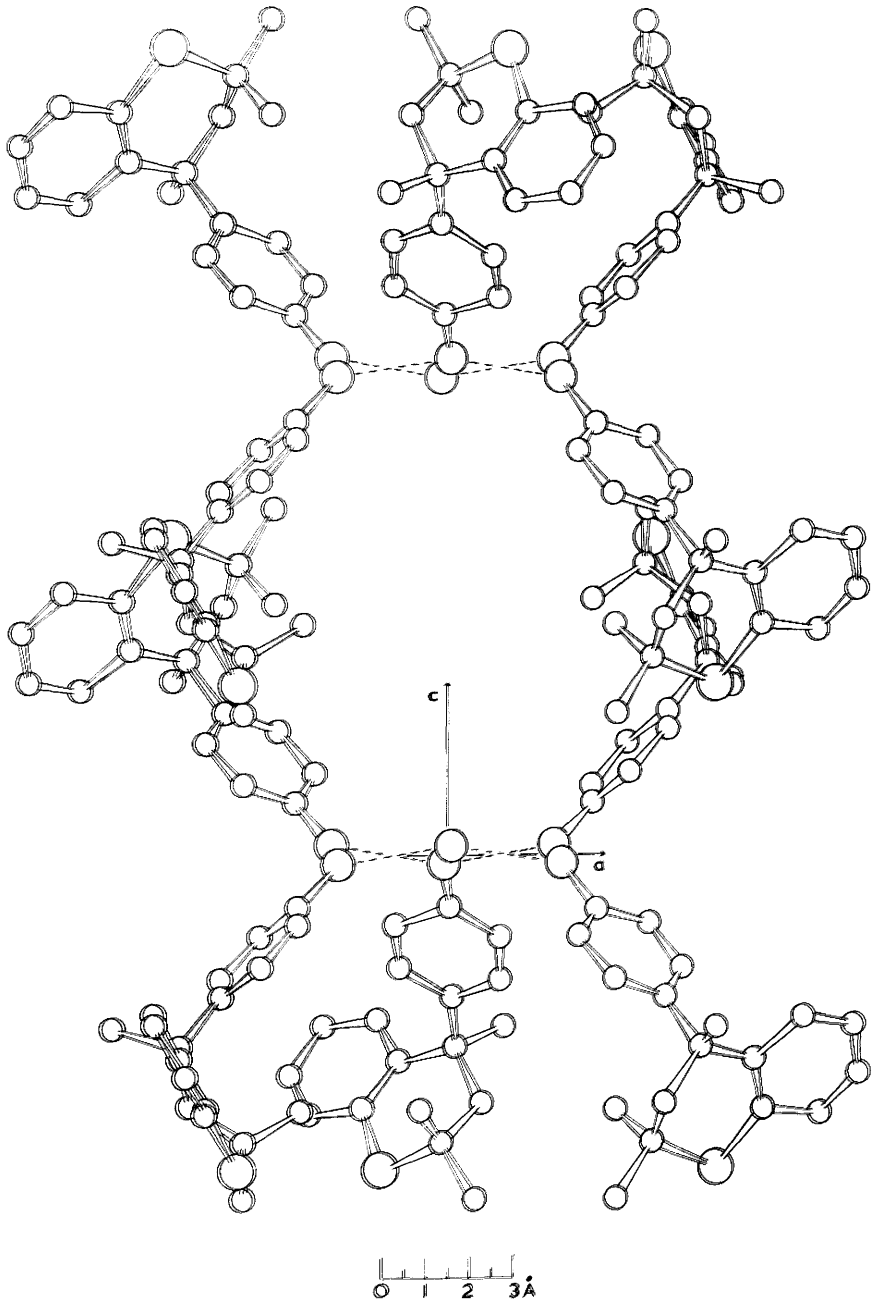

c
a
0 1 2 3Å

FIGURE 3.5

The packing of the molecules as projected on (010). Two molecules of the host, which lie directly above and below the cavity as viewed in this direction, have been excluded apart from their hydroxyl oxygen atoms.


c
a
0 1 2 3Å

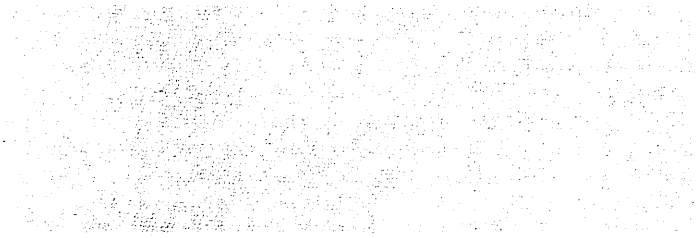
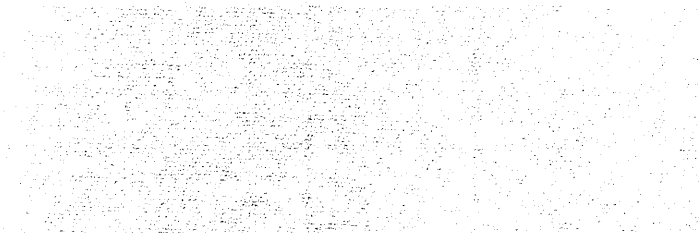


FIGURE 3.6

A section through the van der Waals' surface of the cavity.



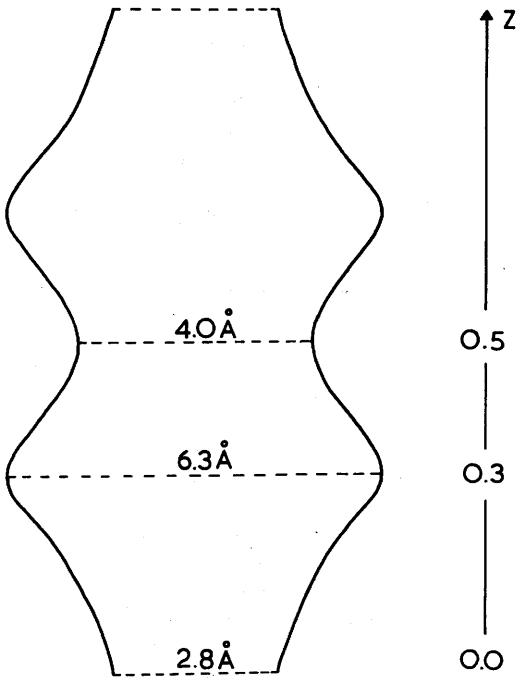

Z
4.0Å
6.3Å
2.8Å
0.5
0.3
0.0

TABLE 3.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	18 C + 2 O	0.48
2	18 C + 2 O	0.305
3	18 C + 2 O	0.255
4	18 C + 2 O	0.212
5	18 C + 2 O	0.207

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layer scales, unit weights	0.163
2	"	0.159
3	"	0.157
4	As above, weighting scheme 1 applied	0.154
5	Block diagonal, individual anisotropic temperature factors, overall scale factor, weighting scheme 2 applied	0.128
6	"	0.122
7	"	0.119
8	"	0.118

TABLE 3.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
O(1)	0.2605 ± 1	0.0865 ± 1	0.6249 ± 4
C(2)	0.2244 ± 2	0.1107 ± 2	0.5937 ± 5
C(3)	0.2597 ± 2	0.1648 ± 2	0.5183 ± 4
C(4)	0.2869 ± 1	0.1579 ± 1	0.4002 ± 5
C(5)	0.3527 ± 2	0.1179 ± 2	0.3544 ± 5
C(6)	0.3770 ± 2	0.0844 ± 2	0.3816 ± 5
C(7)	0.3612 ± 2	0.0520 ± 2	0.4885 ± 5
C(8)	0.3217 ± 2	0.0536 ± 2	0.5679 ± 5
C(9)	0.2971 ± 2	0.0873 ± 2	0.5388 ± 5
C(10)	0.3123 ± 2	0.1200 ± 2	0.4321 ± 4
C(11)	0.2432 ± 1	0.1327 ± 1	0.2971 ± 5
C(12)	0.2150 ± 2	0.1616 ± 2	0.2551 ± 5
C(13)	0.1739 ± 2	0.1395 ± 2	0.1647 ± 5
C(14)	0.1596 ± 2	0.0875 ± 2	0.1082 ± 5
C(15)	0.1881 ± 2	0.0589 ± 2	0.1454 ± 5
C(16)	0.2287 ± 1	0.0813 ± 1	0.2368 ± 5
C(17)	0.3350 ± 2	0.2179 ± 2	0.3641 ± 5
C(18)	0.2089 ± 2	0.1262 ± 2	0.7145 ± 6
C(19)	0.1716 ± 2	0.0647 ± 2	0.5294 ± 5
O(20)	0.1180 ± 2	0.0635 ± 2	0.0210 ± 4

TABLE 3.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
O(1)	0.0425 12	0.0426 12	0.0286 16	0.0294 20	0.0160 20	0.0539 20
C(2)	0.0340 14	0.0294 13	0.0189 19	0.0080 22	0.0069 23	0.0335 23
C(3)	0.0351 13	0.0233 12	0.0186 19	-0.0049 20	-0.0053 22	0.0315 21
C(4)	0.0283 13	0.0212 11	0.0251 20	0.0041 21	0.0049 21	0.0224 20
C(5)	0.0354 15	0.0408 16	0.0329 23	-0.0129 27	-0.0065 26	0.0474 26
C(6)	0.0388 16	0.0492 19	0.0414 26	-0.0184 31	-0.0109 29	0.0591 30
C(7)	0.0403 16	0.0388 16	0.0465 26	-0.0183 29	-0.0257 30	0.0537 28
C(8)	0.0403 16	0.0305 14	0.0376 24	0.0090 26	-0.0139 28	0.0395 25
C(9)	0.0297 13	0.0270 13	0.0226 20	-0.0019 22	-0.0089 22	0.0280 21
C(10)	0.0288 12	0.0265 12	0.0187 19	-0.0098 21	-0.0097 21	0.0292 20
C(11)	0.0301 13	0.0246 12	0.0195 19	0.0018 20	0.0088 21	0.0324 20
C(12)	0.0416 15	0.0310 13	0.0210 20	-0.0024 22	-0.0057 25	0.0475 24
C(13)	0.0426 16	0.0377 15	0.0262 21	0.0039 25	-0.0008 26	0.0562 27

C(14)	0.0317 13	0.0322 13	0.0166 19	0.0022. 22	-0.0031 22	0.0326 22
C(15)	0.0398 15	0.0288 13	0.0186 19	-0.0059 22	-0.0060 24	0.0403 23
C(16)	0.0356 14	0.0280 12	0.0206 20	-0.0049 21	-0.0053 23	0.0400 22
C(17)	0.0379 15	0.0257 13	0.0331 23	0.0123 24	0.0082 26	0.0200 24
C(18)	0.0585 22	0.0486 20	0.0299 26	0.0020 32	0.0222 34	0.0555 35
C(19)	0.0366 16	0.0347 15	0.0361 25	0.0046 28	0.0034 28	0.0195 26
O(20)	0.0465 14	0.0485 13	0.0305 17	-0.0078 22	-0.0250 22	0.0461 23

TABLE 3.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES

H	K	L	F OBS	F CALC
4	1	0	149,1	165,1
7	1	0	103,6	121,3
10	1	0	146,3	159,0
13	1	0	40,9	38,0
16	1	0	40,1	59,1
19	1	0	24,9	22,0
22	1	0	9,7	7,8
25	1	0	25,1	23,3
28	1	0	6,1	4,3
2	2	0	100,6	124,4
5	2	0	82,0	108,4
8	2	0	17,6	6,5
11	2	0	6,3	11,0
14	2	0	44,0	44,7
17	2	0	22,7	21,1
20	2	0	13,9	11,4
23	2	0	29,0	26,8
26	2	0	17,3	16,0
0	3	0	245,2	299,6
3	3	0	229,6	276,5
6	3	0	50,6	44,2
9	3	0	44,2	26,0
12	3	0	20,5	32,9
15	3	0	55,5	44,3
18	3	0	22,9	18,0
21	3	0	35,3	32,6
24	3	0	25,9	23,2
27	3	0	29,4	29,7
1	4	0	121,7	144,4
4	4	0	45,2	43,5
7	4	0	107,9	104,5
10	4	0	33,2	21,9
13	4	0	111,2	119,0
16	4	0	9,4	7,3
19	4	0	7,2	6,3
22	4	0	43,2	36,4
25	4	0	11,5	10,8
2	5	0	135,2	157,3
5	5	0	39,8	46,9
8	5	0	91,2	87,0
11	5	0	16,4	25,6
14	5	0	32,5	27,8
17	5	0	13,3	12,4
20	5	0	16,5	18,1
23	5	0	15,7	9,2
0	6	0	140,5	198,9
3	6	0	33,5	30,2
6	6	0	57,2	49,8
9	6	0	7,1	14,3
12	6	0	8,2	9,2
15	6	0	64,8	58,8
18	6	0	50,7	51,0
24	6	0	7,0	9,2
1	7	0	13,2	5,5
4	7	0	141,1	183,4
7	7	0	60,8	60,7
10	7	0	48,5	50,5
13	7	0	26,3	25,4
16	7	0	49,2	42,2
19	7	0	23,6	24,0
22	7	0	17,2	16,1
2	8	0	81,0	71,6
5	8	0	70,2	62,8
8	8	0	29,2	23,3
11	8	0	103,7	110,2
14	8	0	31,6	30,6
17	8	0	35,7	32,3
20	8	0	29,4	25,4
23	8	0	8,6	9,6
0	9	0	37,7	23,9
3	9	0	40,7	29,2
6	9	0	28,0	24,8
9	9	0	101,2	103,7
12	9	0	43,4	34,5
15	9	0	28,6	22,2
18	9	0	14,7	17,1
21	9	0	7,1	5,4
24	9	0	23,2	24,0
1	10	0	72,1	74,5
4	10	0	31,8	32,2
7	10	0	31,9	17,0
10	10	0	37,0	31,7
13	10	0	37,0	31,7
16	10	0	22,2	20,3
19	10	0	9,6	11,8
22	10	0	12,1	12,3
2	11	0	94,1	94,4
5	11	0	57,6	50,2
8	11	0	67,4	59,7
11	11	0	14,4	18,6
14	11	0	8,9	11,2
20	11	0	7,4	1,7
0	12	0	51,0	44,4
3	12	0	40,3	44,8
6	12	0	73,9	72,1
9	12	0	13,1	7,6
12	12	0	53,4	48,1
15	12	0	46,4	44,4
18	12	0	12,1	13,1
21	12	0	3,6	2,7
4	13	0	10,1	10,4
7	13	0	57,4	57,2
10	13	0	90,6	86,0
13	13	0	22,3	19,0
16	13	0	27,4	26,0
19	13	0	7,1	8,1
2	14	0	27,0	26,2
5	14	0	56,3	51,9
8	14	0	75,2	69,8
11	14	0	3,4	2,9
17	14	0	23,9	22,0
20	14	0	18,4	20,9
0	15	0	23,0	19,9
3	15	0	18,5	11,1
6	15	0	23,2	22,4
9	15	0	49,1	51,3
12	15	0	24,4	21,3
15	15	0	8,1	7,2
18	15	0	3,3	5,3
1	16	0	20,7	17,0
4	16	0	26,3	15,9
7	16	0	8,2	1,0
10	16	0	55,6	52,3
13	16	0	41,2	41,3
16	16	0	25,6	26,9
2	17	0	3,4	2,4
5	17	0	14,5	12,8
8	17	0	5,1	2,6
11	17	0	45,3	44,1
14	17	0	35,8	32,2
17	17	0	7,6	8,4
0	18	0	58,9	57,5
3	18	0	12,3	12,5
6	18	0	12,5	16,4
9	18	0	25,4	21,1
12	18	0	13,4	13,5
15	18	0	20,6	21,9
1	19	0	17,3	20,3
4	19	0	3,6	1,7
7	19	0	51,6	49,5
10	19	0	5,5	4,2
2	20	0	28,1	27,1
5	20	0	6,5	4,0
11	20	0	25,9	21,4
0	21	0	44,7	47,6
3	21	0	33,8	31,2
6	21	0	7,4	7,6
9	21	0	33,4	31,8
12	21	0	6,3	4,3
15	21	0	25,0	21,4
1	22	0	9,2	9,2
4	22	0	26,4	25,8
7	22	0	11,6	11,9
10	22	0	6,4	6,3
13	22	0	12,5	11,9
16	22	0	15,3	14,9
2	23	0	11,4	13,0
5	23	0	6,1	5,3
8	23	0	11,5	12,7
11	23	0	25,2	24,8
14	23	0	10,9	13,6
17	23	0	5,1	5,9
0	24	0	10,9	13,6
3	24	0	10,9	13,6
6	24	0	10,2	9,9
9	24	0	6,3	8,3
12	24	0	51,9	43,0
15	24	0	14,9	13,0
7	25	0	25,1	25,1
0	26	0	20,3	17,2
3	26	0	11,5	12,7
6	26	0	0,4	6,3
9	26	0	11,8	7,6
12	26	0	30,9	29,6
3	27	0	33,8	31,8
6	27	0	12,5	11,9
9	27	0	15,6	13,6
12	27	0	30,9	27,7
15	27	0	9,2	8,4
6	28	0	74,2	80,0
9	28	0	11,9	3,1
12	28	0	73,8	72,2
15	28	0	39,6	43,3
18	28	0	22,6	22,5
21	28	0	23,9	27,9
24	28	0	3,1	5,5
27	28	0	6,1	4,3
6	29	0	23,9	27,9
9	29	0	23,9	22,6
12	29	0	12,7	13,7
15	29	0	12,5	11,9
18	29	0	6,3	8,3
21	29	0	15,6	14,6
24	29	0	6,3	4,3
5	30	0	4,5	6,8
8	30	0	11,4	13,5
11	30	0	38,6	32,6
14	30	0	24,0	28,6
17	30	0	16,0	11,5
20	30	0	45,0	36,4
23	30	0	22,0	22,3
26	30	0	12,2	13,3
5	31	0	45,0	46,6
8	31	0	72,7	59,2
11	31	0	25,1	25,1
14	31	0	43,9	42,5
17	31	0	14,5	15,4
20	31	0	13,5	13,2
23	31	0	19,3	19,7
26	31	0	6,3	8,6
29	31	0	22,0	20,5
32	31	0	6,3	5,9
-13	28	1	11,3	9,6
-13	34	1	18,3	21,2
-14	15	1	73,4	75,3
-14	18	1	55,2	52,6
-14	21	1	80,1	83,1
-14	24	1	118,3	107,9
-14	27	1	66,3	58,0
-14	30	1	4,5	6,8
-14	33	1	11,4	13,5
-15	17	1	38,6	32,6
-15	20	1	24,0	28,6
-15	23	1	16,0	11,5
-15	26	1	45,0	36,4
-15	29	1	22,0	22,3
-15	32	1	12,2	13,3
-16	19	1	45,0	46,6
-16	22	1	72,7	59,2
-16	25	1	8,5	11,2
-16	28	1	43,9	42,5
-16	31	1	14,5	15,4
-16	34	1	13,5	13,2
-17	21	1	19,3	19,7
-17	24	1	79,5	69,0
-17	27	1	8,5	7,6
-17	30	1	93,0	85,4
-17	33	1	23,0	30,2
-18	20	1	9,0	11,1
-18	23	1	32,2	28,5
-18	26	1	88,5	75,7
-18	29	1	12,1	11,0
-18	32	1	11,5	10,6
-19	22	1	9,3	10,6
-19	25	1	40,6	41,6
-19	28	1	45,4	41,6
-19	31	1	13,2	14,2
-19	34	1	6,1	4,9
-20	24	1	65,0	56,7
-20	27	1	84,8	76,6
-20	33	1	7,7	9,1
-21	23	1	34,2	31,4
-21	26	1	24,3	23,4
-21	29	1	13,6	19,9
-21	32	1	2,5	4,3
-22	31	1	5,4	4,8
-23	25	1	11,0	11,4
-23	27	1	7,5	8,9
-23	30	1	2,9	2,4
-23	33	1	7,5	10,1
-24	26	1	27,1	25,3
-24	29	1	21,7	26,2
-24	32	1	52,3	55,7
-25	28	1	8,0	10,1
-26	27	1	10,1	9,1
-26	30	1	24,7	22,5
-27	29	1	41,8	40,9
-28	31	1	11,1	14,9
-29	30	1	19,5	23,7
5	0	2	115,5	117,7
8	0	2	165,9	174,1
11	0	2	7,7	7,4
14	0	2	44,6	40,7
17	0	2	46,2	45,5
20	0	2	3,4	5,4
23	0	2	7,5	8,6
26	0	2	4,0	4,1
29	0	2	1,6	4,2
0	1	2	77,2	107,4
3	1	2	399,7	474,7
6	1	2	170,9	180,2
9	1	2	20,1	19,7
12	1	2	56,0	65,7
15	1	2	5,1	7,6
18	1	2	89,2	80,4
21	1	2	38,4	32,4
24	1	2	5,3	8,6
27	1	2	11,4	10,6
1	2	2	139,4	173,4
4	2	2	211,6	220,0
7	2	2	45,1	41,0
10	2	2	16,7	19,4
13	2	2	125,1	111,8
16	2	2	101,0	89,2
19	2	2	41,6	48,6
22	2	2	61,4	47,9
25	2	2	28,3	26,2
28	2	2	26,3	26,7
31	2	2	24,6	26,2
34	2	2	9,7	12,3
2	3	2	43,9	40,3
5	3	2	171,2	182,1
8	3	2	19,4	32,2
11	3	2	95,5	90,2
14	3	2	37,0	32,3
17	3	2	79,0	74,7
20	3	2	61,5	55,1
23	3	2	20,2	17,4
26	3	2	25,6	29,4
0	4	2	246,0	240,9
3	4	2	129,6	141,8
6	4	2	19,9	13,6
9	4	2	33,0	32,4
12	4	2	11,0	2,4
18	4	2	22,9	26,5
21	4	2	34,4	29,4
24	4	2	45,5	42,6
27	4	2	22,2	27,2
1	5	2	72,9	61,2
4	5	2	58,4	55,7
7	5	2	15,5	10,3
10	5	2	51,3	57,3
13	5	2	76,7	73,7
16	5	2	65,1	59,6
22	5	2	4,3	2,5
25	5	2	13,2	14,4
0	6	2	145,1	144,6
3	6	2	144,1	172,9
6	6	2	116,1	113,7
9	6	2	31,1	28,6
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-22	28	3	14,4	11,4
-22	31	3	20,2	18,5
-23	29	3	20,2	21,3
-23	32	3	25,5	27,2
-24	30	3	14,4	15,1
-25	31	3	15,0	12,0
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4	0	4	96,0	102,8
7	0	4	112,6	97,0
10	0	4	97,4	90,5
13	0	4	26,3	17,1
16	0	4	5,5	11,3
19	0	4	59,7	54,4
22	0	4	15,2	16,5
25	0	4	13,1	10,6
28	0	4	16,2	17,7
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8	1	4	87,5	87,2
11	1	4	24,3	20,4
14	1	4	35,4	28,9
17	1	4	112,7	97,3
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23	1	4	47,7	38,0
26	1	4	2,9	3,9
29	1	4	6,7	2,3
4	2	4	62,7	58,0
7	2	4	160,1	164,8
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13	2	4	41,2	32,5
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19	2	4	51,6	44,9
22	2	4	74,4	61,7
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7	3	4	108,4	133,5
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16	3	4	29,2	29,3
19	3	4	15,3	16,0
22	3	4	20,4	20,9
25	3	4	69,6	67,6
28	3	4	91,8	100,6
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34	3	4	28,8	25,4
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40	3	4	87,4	79,6
43	3	4	68,0	61,3
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73	3	4	7,9	10,7
76	3	4	12,5	13,7
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82	3	4	5,6	6,1
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H	K	L	F OBS	F CALC
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15	0	6	48.1	52.6
18	0	6	18.2	14.5
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7	1	6	29.1	23.2
10	1	6	25.6	19.2
13	1	6	19.5	18.0
16	1	6	22.9	25.7
19	1	6	25.2	25.6
22	1	6	14.1	15.3
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5	2	6	15.7	19.9
8	2	6	13.5	15.9
11	2	6	27.4	28.5
14	2	6	10.6	12.3
17	2	6	22.2	23.9
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12	3	6	17.3	15.4
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19	4	6	4.3	2.2
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11	5	6	29.9	27.6
14	5	6	44.5	43.6
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10	7	6	3.7	6.1
13	7	6	11.6	10.2
16	7	6	5.2	3.4
2	8	6	53.2	63.7
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8	8	6	27.6	26.7
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17	8	6	3.0	5.1
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9	9	6	41.9	51.2
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13	10	6	16.7	16.4
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13	12	6	26.6	26.3
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15	13	6	11.6	12.3
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6	18	6	6.1	4.4
9	18	6	25.8	31.8
12	18	6	7.0	6.5
4	19	6	8.0	6.0
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8	20	6	19.7	22.9
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2	23	6	8.9	11.9
5	23	6	19.7	19.6
3	24	6	32.7	30.5
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-5	10	6	25.3	26.9
-5	13	6	62.7	64.3
-5	16	6	43.7	46.7
-5	19	6	24.4	22.5
-5	22	6	7.4	4.2
-5	25	6	15.1	14.3
-6	9	6	75.6	87.0
-6	12	6	49.2	53.7
-6	15	6	39.2	41.6
-6	18	6	16.7	18.0
-6	21	6	21.9	19.6
-6	24	6	5.0	3.2
-6	27	6	35.9	32.9
-7	8	6	19.6	24.9
-7	11	6	72.1	78.7
-7	14	6	41.1	38.4
-7	17	6	133.1	134.8
-7	20	6	9.3	13.3
-7	23	6	29.1	25.8
-7	26	6	12.3	11.3

H	K	L	F OBS	F CALC
-14	15	7	45.7	51.1
-14	21	7	24.9	20.9
-14	24	7	7.4	8.4
-14	27	7	13.7	11.1
-15	20	7	40.0	37.0
-15	23	7	25.5	25.8
-15	26	7	8.1	6.8
-15	29	7	19.3	22.8
-16	22	7	21.2	17.0
-16	25	7	14.3	14.6
-16	28	7	15.2	15.9
-17	21	7	11.1	8.3
-17	24	7	15.7	13.7
-17	27	7	18.6	19.6
-18	20	7	29.8	30.8
-18	23	7	12.2	11.1
-18	29	7	22.9	23.5
-19	22	7	28.7	31.7
-20	21	7	6.5	2.5
-20	24	7	28.9	26.6
2	0	8	19.0	17.6
5	0	8	20.9	21.0
8	0	8	14.8	14.5
11	0	8	8.5	2.9
14	0	8	21.2	22.1
17	0	8	20.6	17.5
23	0	8	33.6	35.3
0	1	8	49.2	66.5
3	1	8	5.5	5.6
6	1	8	32.2	35.7
9	1	8	15.5	17.6
12	1	8	61.5	66.3
15	1	8	37.1	37.0
21	1	8	30.8	32.9
24	1	8	13.9	15.6
1	2	8	31.4	41.8
4	2	8	47.1	58.7
7	2	8	12.0	11.7
10	2	8	11.3	8.4
13	2	8	24.0	16.7
16	2	8	36.7	39.1
19	2	8	20.7	19.4
22	2	8	9.7	6.5
2	3	8	23.1	24.7
5	3	8	8.3	3.0
8	3	8	49.1	51.1
11	3	8	38.3	39.7
14	3	8	19.6	9.0
17	3	8	4.8	5.0
0	4	8	25.1	34.5
3	4	8	40.0	42.3
6	4	8	19.8	23.1
9	4	8	34.4	32.2
12	4	8	24.6	29.7
18	4	8	29.9	27.2
21	4	8	9.3	7.5
1	5	8	61.6	90.0
4	5	8	67.2	80.5
7	5	8	15.5	8.1
10	5	8	48.9	46.4
13	5	8	22.4	21.4
19	5	8	3.9	2.4
2	6	8	39.0	45.5
5	6	8	70.7	89.0
8	6	8	4.5	2.1
11	6	8	20.2	17.6
14	6	8	16.5	11.8
17	6	8	4.3	3.1
20	6	8	5.4	3.9
0	7	8	70.6	95.5
3	7	8	48.3	61.5
6	7	8	19.7	13.6
9	7	8	17.3	23.6
12	7	8	19.5	17.1
15	7	8	16.1	11.1
18	7	8	27.6	29.9
1	8	8	27.4	20.4
4	8	8	19.2	20.3
7	8	8	12.9	9.4
10	8	8	14.3	11.7
13	8	8	4.9	2.2
16	8	8	11.1	12.5
2	9	8	39.9	39.2
5	9	8	6.4	6.8
8	9	8	5.0	6.2
11	9	8	33.4	34.9
14	9	8	25.9	25.5
17	9	8	12.2	10.3
0	10	8	46.6	57.9
3	10	8	16.4	12.0
6	10	8	18.7	18.5
12	10	8	21.2	19.6
15	10	8	25.8	22.2
18	10	8	32.9	33.2
1	11	8	11.5	12.2
4	11	8	7.0	2.3
7	11	8	11.3	8.5
10	11	8	30.5	34.1
13	11	8	16.7	13.2
16	11	8	11.4	5.1
2	12	8	72.1	83.1
8	12	8	12.2	7.0
11	12	8	31.6	29.8
14	12	8	10.4	9.5
0	13	8	76.3	86.5
3	13	8	47.8	44.5
6	13	8	48.0	51.1
9	13	8	18.9	14.0
12	13	8	34.2	36.4
15	13	8	20.6	21.4
1	14	8	24.6	19.9
4	14	8	21.4	19.2
10	14	8	12.1	9.6
13	14	8	11.2	7.3
2	15	8	16.7	6.4
5	15	8	20.8	21.1
11	15	8	3.6	0.3
0	16	8	40.1	41.8
3	16	8	19.1	16.3
6	16	8	21.5	19.5
12	16	8	8.7	8.9
1	17	8	57.0	64.6
4	17	8	28.1	24.2
7	17	8	21.2	21.3
10	17	8	16.5	13.2
0	19	8	19.0	17.1
3	19	8	16.3	13.2
6	19	8	7.2	7.9
1	20	8	17.0	17.8
4	20	8	3.5	2.1
7	20	8	18.3	22.6
0	22	8	14.1	10.7
3	23	8	23.2	26.0
-1	3	8	30.1	43.2
-1	6	8	21.3	29.2
-1	9	8	42.4	54.3
-1	12	8	94.2	120.0
-1	15	8	45.2	52.3
-1	18	8	20.5	18.2
-1	21	8	25.2	27.4
-1	24	8	26.4	32.2
-2	5	8	12.7	6.2

H	K	L	F OBS	F CALC
-2	8	8	22.5	19.5
-2	11	8	137.0	164.2
-2	14	8	20.2	15.0
-2	17	8	13.4	12.8
-2	23	8	24.2	20.9
-3	4	8	7.5	9.0
-3	7	8	15.4	20.2
-3	10	8	102.6	142.6
-3	13	8	25.9	22.9
-3	16	8	19.5	15.6
-3	19	8	21.0	15.9
-3	25	8	15.1	13.0
-4	6	8	34.7	41.9
-4	9	8	14.6	16.0
-4	12	8	14.3	22.3
-4	15	8	39.2	39.7
-4	18	8	62.6	62.6
-4	21	8	20.9	16.8
-4	24	8	25.4	24.1
-5	3	8	9.6	12.1
-5	11	8	38.5	47.6
-5	17	8	64.3	78.3
-5	20	8	50.9	53.2
-5	23	8	19.1	19.4
-5	26	8	28.9	37.0
-6	7	8	6.2	6.1
-6	10	8	4.1	8.3
-6	13	8	52.1	56.4
-6	16	8	13.5	15.6
-6	19	8	19.4	21.8
-6	25	8	24.4	19.6
-7	9	8	10.6	10.6
-7	12	8	14.0	9.5
-7	15	8	32.9	39.1
-7	18	8	30.3	39.9
-7	21	8	29.0	35.6
-7	24	8	9.2	8.8
-8	6	8	9.4	4.6
-8	12	8	8.0	4.9
-8	18	8	38.9	47.3
-8	21	8	4.9	2.1
-8	24	8	16.6	16.5
-9	7	8	15.3	17.3
-9	13	8	61.9	63.5
-9	16	8	23.1	26.1
-9	19	8	17.2	15.0
-9	22	8	27.3	30.5
-10	8	8	13.6	12.0
-10	11	8	23.0	24.7
-10	14	8	8.0	4.9
-10	17	8	38.9	47.3
-10	20	8	4.9	2.1
-10	23	8	16.6	16.5
-11	4	8	9.4	4.6
-11	10	8	4.1	8.3
-11	13	8	52.1	56.4
-11	16	8	13.5	15.6
-11	19	8	19.4	21.8
-11	25	8	24.4	19.6
-12	9	8	10.6	10.6
-12	12	8	14.0	9.5
-12	15	8	32.9	39.1
-12	18	8	30.3	39.9
-12	21	8	29.0	35.6
-12	24	8	9.2	8.8
-13	6	8	9.4	4.6
-13	12	8	8.0	4.9
-13	18	8	38.9	47.3
-13	21	8	4.9	2.1
-13	24	8	16.6	16.5
-14	7	8	15.3	17.3
-14	13	8	61.9	63.5
-14	16	8	23.1	26.1
-14	19	8	17.2	15.0
-14	22	8	27.3	30.5
-15	8	8	13.6	12.0
-15	11	8	23.0	24.7
-15	14	8	8.0	4.9
-15	17	8	38.9	47.3
-15	20	8	4.9	2.1
-15	23	8	16.6	16.5
-16	7	8	15.3	17.3
-16	13	8	61.9	63.5
-16	16	8	23.1	26.1
-16	19	8	17.2	15.0
-16	22	8	27.3	30.5
-17	8	8	13.6	12.0
-17	11	8	23.0	24.7
-17	14	8	8.0	4.9
-17	17	8	38.9	47.3
-17	20	8	4.9	2.1
-17	23	8	16.6	16.5
-18	7	8	15.3	17.3
-18	13	8	61.9	63.5
-18	16	8	23.1	26.1
-18	19	8	17.2	15.0
-18	22	8	27.3	30.5
-19	8	8	13.6	12.0
-19	11	8	23.0	24.7
-19	14	8	8.0	4.9
-19	17	8	38.9	47.3
-19	20	8	4.9	2.1
-19	23	8	16.6	16.5
-20	7	8	15.3	17.3
-20	13	8	61.9	63.5
-20	16	8	23.1	26.1
-20	19	8	17.2	15.0
-20	22	8	27.3	30.5
11	0	9	33.0	30.4
14	0	9	9.2	6.9
17	0	9	19.1	16.2
0	1	9	20.0	21.9
3	1	9	11.9	8.7
6	1	9	28.3	29.8
9	1	9	37.1	40.2
12	1	9	7.7	5.8
15	1	9	26.9	34.9
18	1	9	20.6	26.9
21	1	9	24.1	17.0
1	2	9	6.5	3.1
4	2	9	11.6	10.2
7	2	9	50.6	65.3
10	2	9	61.8	63.0
13	2	9	10.5	6.9
16	2	9	26.4	27.1
19	2	9	37.0	36.9
22	2	9	32.2	30.7
2	3	9	17.2	15.1
5	3	9	20.5	20.3
8	3	9	19.2	16.8
11	3	9	23.7	20.1
14	3	9	6.6	3.1
17	3	9	17.2	17.7
0	4	9	3.6	2.0
3	4	9	10.8	8.0
6	4	9	18.5	18.3
9	4	9	9.0	8.6
12	4	9	17.4	14.7
15	4	9	30.9	32.6
18	4	9	7.5	6.0
21	4	9	11.8	11.4
1	5	9	2.7	3.2
4	5	9	5.9	2.4
7	5	9	23.5	22.3
10	5	9	20.9	23.3
13	5	9	4.9	9.1
16	5	9	6.7	4.4
19	5	9	10.5	6.9
2	6	9	17.1	25.8
5	6	9	23.8	27.7
8	6	9	80.8	108.2
11	6	9	68.8	85.9
14	6	9	18.8	22.4
17	6	9	38.1	37.2
20	6	9	11.1	12.3
0	7	9	20.9	21.4
3	7	9	11.7	10.6
6	7	9	48.5	75.0
9	7	9	23.2	28.9
12	7	9	10.1	9.1
15	7	9	12.5	9.9
18	7	9	8.2	5.5
21	7	9	6.7	5.3
1	8	9	21.2	19.9
4	8	9	36.2	40.5
7	8	9	22.2	23.3
10	8	9	22.0	23.1
13	8	9	20.5	17.6
16	8	9	28.5	34.3
19	8	9	41.6	43.1
22	8	9	14.8	16.8
2	9	9	31.4	42.6
5	9	9	16.1	10.0
8	9	9	47.7	50.6
11	9	9	35.2	33.6
14	9	9	21.0	18.5
17	9	9	7.2	7.3
0	10	9	16.0	15.2
3	10	9	10.4	10.7
6	10	9	13.2	12.5
9	10	9	39.0	53.0
12	10	9	42.1	55.2
15	10	9	49.9	63.4
18	10	9	30.6	39.2
21	10	9	17.8	19.7
1	11	9	25.8	31.6
4	11	9	40.1	42.6
7	11	9	20.5	20.8
10	11	9	47.5	57.1
13	11	9	6.9	5.4
16	11	9	30.5	31.7
19	11	9	38.3	47.9
22	11	9	9.8	9.8
2	12	9	32.2	28.5
5	12	9	16.0	10.8
8	12	9	14.4	10.0
11	12	9	15.7	15.9
14	12	9	48.0	99.1
17	12	9	4.7	2.6
20	12	9	22.8	22.8
23	12	9	21.4	19.6
3	13	9	9.4	6.5
6	13	9	26.3	26.9
9	13	9	23.1	20.9
12	13	9	15.6	13.7
15	13	9	6.5	1.7
18	13	9	24.2	23.7
21	13	9	16.8	16.0
24	13	9	3.4	4.4
1	14	9	31.8	39.7
4	14	9	24.0	27.4
7	14	9	7.1	7.7
10	14	9	31.8	36.9
13	14	9	7.7	2.6
16	14	9	15.7	15.9
19	14	9	48.0	99.1
22	14	9	4.7	2.6
2	15	9	22.8	22.8
5	15	9	21.4	19.6
11	15	9	9.4	6.5
0	16	9	26.3	26.9
3	16	9	23.1	20.9
6	16	9	15.6	13.7
12	16	9	6.5	1.7
1	17	9	24.2	23.7
4	17	9	16.8	16.0
7	17	9	3.4	4.4
2	18	9	31.8	39.7
5	18	9	24.0	27.4
8	18	9	7.1	7.7
11	18	9	31.8	36.9
14	18	9	7.7	2.6
17	18	9	15.7	15.9
20	18	9	48.0	99.1
23	18	9	4.7	2.6
3	19	9	22.8	22.8
6	19	9	21.4	19.6
12	19	9	9.4	6.5
15	19	9	26.3	26.9
18	19	9	23.1	20.9
21	19	9	15.6	13.7
24	19	9	6.5	1.7
4	20	9	24.2	23.7
7	20	9	16.8	16.0
10	20	9	3.4	4.4
5	21	9	31.8	39.7
8	21	9	24.0	27.4
11	21	9	7.1	7.7
14	21	9	31.8	36.9
17	21	9	7.7	2.6
20	21	9	15.7	15.9
23	21	9	48.0	99.1
6	22	9	4.7	2.6
9	22	9	22.8	22.8
12	22	9	21.4	19.6
18	22	9	9.4	6.5
21	22	9	26.3	26.9
24	22	9	23.1	20.9
7	23	9	15.6	13.7
10	23	9	6.5	1.7
13	23	9	24.2	23.7
16	23	9	16.8	16.0
19	23	9	3.4	4.4
8	24	9	31.8	39.7
11	24	9	24.0	27.4
14	24	9	7.1	7.7
17	24	9	31.8	36.9
20	24	9	7.7	2.6
23	24	9	15.7	15.9
9	25	9	48.0	99.1
12	25	9	4.7	2.6
15	25	9	22.8	22.8
18	25	9	21.4	19.6
24	25	9	9.4	6.5
10	26	9	26.3	26.9
13	26	9	23.1	20.9
16	26	9	15.6	13.7
22	26	9	6.5	1.7
12	27	9	24.2	23.7
15	27	9	16.8	16.0
18	27	9	3.4	4.4
14	28	9	31.8	39.7
17	28	9	24.0	27.4
20	28	9	7.1	7.7
16	29	9	31.8	36.9
19	29	9	7.7	2.6
22	29	9	15.7	15.9
18	30	9	48.0	99.1
21	30	9	4.7	2.6
24	30	9	22.8	22.8
20	31	9

TABLE 3.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X'	Y'	Z
O(1)	6.077 ± 3	-1.179 ± 3	6.834 ± 4
C(2)	5.235 ± 4	-0.039 ± 4	6.492 ± 5
C(3)	6.059 ± 4	0.940 ± 4	5.667 ± 5
C(4)	6.694 ± 3	0.388 ± 3	4.376 ± 5
C(5)	8.227 ± 4	-1.573 ± 4	3.875 ± 6
C(6)	8.796 ± 4	-2.805 ± 4	4.173 ± 6
C(7)	8.426 ± 4	-3.465 ± 4	5.342 ± 6
C(8)	7.506 ± 4	-2.889 ± 4	6.210 ± 6
C(9)	6.930 ± 4	-1.650 ± 4	5.892 ± 5
C(10)	7.285 ± 4	-0.975 ± 4	4.725 ± 5
C(11)	5.674 ± 3	0.299 ± 3	3.249 ± 5
C(12)	5.016 ± 4	1.456 ± 4	2.790 ± 5
C(13)	4.058 ± 4	1.415 ± 3	1.801 ± 6
C(14)	3.723 ± 4	0.208 ± 4	1.184 ± 6
C(15)	4.389 ± 4	-0.947 ± 4	1.590 ± 5
C(16)	5.336 ± 3	-0.891 ± 3	2.589 ± 5
C(17)	7.814 ± 4	1.359 ± 4	3.982 ± 6
C(18)	4.874 ± 5	0.585 ± 5	7.813 ± 7
C(19)	4.004 ± 4	-0.570 ± 5	5.789 ± 6
O(20)	2.753 ± 4	0.120 ± 4	0.230 ± 5

TABLE 3.6

BOND LENGTHS AND E.S.D.S.

O(1) - C(2)	1.458 ± 5 Å	C(6) - C(7)	1.393 ± 8 Å
O(1) - C(9)	1.356 ± 6	C(7) - C(8)	1.390 ± 7
C(2) - C(3)	1.523 ± 6	C(8) - C(9)	1.402 ± 6
C(2) - C(18)	1.505 ± 8	C(9) - C(10)	1.394 ± 7
C(2) - C(19)	1.514 ± 6	C(11)- C(12)	1.408 ± 5
C(3) - C(4)	1.541 ± 6	C(11)- C(16)	1.403 ± 5
C(4) - C(10)	1.526 ± 5	C(12)- C(13)	1.377 ± 7
C(4) - C(11)	1.523 ± 6	C(13)- C(14)	1.396 ± 6
C(4) - C(17)	1.535 ± 6	C(14)- C(15)	1.394 ± 5
C(5) - C(6)	1.389 ± 6	C(14)- O(20)	1.363 ± 6
C(5) - C(10)	1.403 ± 6	C(15)- C(16)	1.378 ± 6

TABLE 3.7

INTERBOND ANGLES AND E.S.D.S.

C(2) - O(1) - C(9)	118.2 ± 4°	C(7) - C(8) - C(9)	119.7 ± 5°
O(1) - C(2) - C(3)	108.5 ± 3	O(1) - C(9) - C(8)	114.1 ± 4
O(1) - C(2) - C(18)	104.9 ± 4	O(1) - C(9) - C(10)	125.0 ± 3
O(1) - C(2) - C(19)	107.7 ± 3	C(8) - C(9) - C(10)	120.9 ± 4
C(3) - C(2) - C(18)	109.8 ± 4	C(4) - C(10)- C(5)	120.2 ± 4
C(3) - C(2) - C(19)	114.5 ± 4	C(4) - C(10)- C(9)	121.7 ± 4
C(18)- C(2) - C(19)	111.0 ± 4	C(5) - C(10)- C(9)	118.1 ± 4
C(2) - C(3) - C(4)	116.5 ± 3	C(4) - C(11)- C(12)	120.4 ± 3
C(3) - C(4) - C(10)	106.8 ± 4	C(4) - C(11)- C(16)	124.0 ± 3
C(3) - C(4) - C(11)	111.4 ± 3	C(12)- C(11)- C(16)	115.6 ± 4
C(3) - C(4) - C(17)	106.8 ± 3	C(11)- C(12)- C(13)	122.3 ± 4
C(10)- C(4) - C(11)	112.2 ± 3	C(12)- C(13)- C(14)	120.7 ± 4
C(10)- C(4) - C(17)	109.9 ± 3	C(13)- C(14)- C(15)	118.2 ± 4
C(11)- C(4) - C(17)	109.6 ± 4	C(13)- C(14)- O(20)	122.4 ± 4
C(6) - C(5) - C(10)	121.5 ± 5	C(15)- C(14)- O(20)	119.4 ± 4
C(5) - C(6) - C(7)	119.5 ± 5	C(14)- C(15)- C(16)	120.4 ± 4
C(6) - C(7) - C(8)	120.3 ± 4	C(11)- C(16)- C(15)	122.8 ± 3

TABLE 3.8

INTERMOLECULAR CONTACTS BELOW 4 Å

O(20)....O(20)	ii	2.79 Å	C(15)....C(17)	viii	3.89 Å
C(13)....O(20)	iv	3.60	C(8).....C(6)	vii	3.89
O(1).....C(12)	iii	3.60	C(6).....C(18)	ix	3.90
C(14)....O(20)	iv	3.61	C(16)....C(18)	iii	3.90
C(15)....C(18)	iii	3.65	C(5).....C(18)	ix	3.92
C(14)....O(20)	ii	3.67	C(7).....C(18)	ix	3.92
C(15)....O(20)	ii	3.70	C(6).....C(15)	vii	3.93
C(7).....C(6)	vii	3.71	C(8).....C(7)	vii	3.95
C(17)....C(6)	vi	3.75	C(8).....C(18)	ix	3.96
C(5).....C(12)	viii	3.80	C(7).....C(5)	vii	3.97
C(16)....C(17)	viii	3.82	C(10)....C(18)	ix	3.98
C(6).....C(13)	viii	3.83	C(6).....C(12)	viii	3.98
C(5).....C(13)	viii	3.85	C(13)....C(18)	v	3.98
C(12)....C(19)	v	3.86	O(1).....C(13)	iii	3.99
C(7).....C(16)	vii	3.86	C(18)....O(20)	i	3.99
C(17)....C(7)	vi	3.87	C(9).....C(18)	ix	3.99
C(3).....C(8)	ix	3.88			

Roman numerals refer to the transformations of the fractional coordinates given in Table 3.2.

i	x,	y,	$1 + z$;	vi	$\frac{1}{3} + y$,	$\frac{2}{3} + y - x$,	$\frac{2}{3} - z$;
ii	y,	$y - x$,	$-z$;	vii	$\frac{2}{3} + y - x$,	$\frac{1}{3} - x$,	$\frac{1}{3} + z$;
iii	y,	$y - x$,	$1 - z$;	viii	$\frac{2}{3} - x$,	$\frac{1}{3} - y$,	$\frac{1}{3} - z$;
iv	$x - y$,	x,	$-z$;	ix	$\frac{2}{3} - x$,	$\frac{1}{3} - y$,	$1\frac{1}{3} - z$;
v	$x - y$,	x,	$1 - z$;				

The transformations are applied to the coordinates of the second atom in each case.

TABLE 3.9

MEAN MOLECULAR PLANES

(A) ATOMS DEFINING PLANES

PLANE NO.	ATOMS DEFINING PLANE
1	C(5), C(6) and C(7)
2	O(1), C(4), C(9) and C(10)
3	O(1), C(4), C(5), C(6), C(7), C(8), C(9) and C(10)
4	C(4), C(11), C(12), C(13), C(14), C(15), C(16) and O(20)

(B) PLANE EQUATIONS

PLANE NO.	P	Q	R	S	RMS D
1	-0.7381	-0.4601	-0.4935	-7.2610	0.000
2	-0.7587	-0.4444	-0.4762	-7.3381	0.006
3	-0.7453	-0.4576	-0.4849	-7.2860	0.011
4	0.7113	0.1582	-0.6848	1.8631	0.025

P, Q and R are the direction cosines of the plane normal, S is the plane to origin distance and RMS D is the root mean square deviation of the atoms defining the plane, from the plane, in Angstroms. The plane equation is then

$$PX + QY + RZ = S$$

where X, Y and Z are coordinates in Angstroms referred to standard orthogonal axes.

(C) DEVIATION FROM PLANES (Å)

PLANE NO. / ATOM	1	2	3	4
O(1)	-0.055	-0.004	-0.018	-2.406
C(2)	-	0.292	0.254	-2.592
C(3)	-	-0.376	-0.408	-1.285
C(4)	-0.017	0.003	-0.002	-0.037
C(5)	0.000	-	-0.005	1.087
C(6)	0.000	-	-0.009	1.092
C(7)	0.000	-	0.002	-0.076
C(8)	-0.015	-	0.002	-1.234
C(9)	-0.002	0.007	0.019	-1.230
C(10)	0.000	-0.007	0.011	-0.071
C(11)	-	1.353	1.345	-0.004
C(12)	-	-	-1.091	0.025
C(13)	-	-	-0.403	0.014
C(14)	-	-	1.756	0.007
C(15)	-	-	1.528	0.020
C(16)	-	-	2.741	0.019
C(17)	-	-1.091	3.842	1.184
C(18)	-	-0.341	3.678	-3.654
C(19)	-	1.797	2.461	-3.069
O(20)	-	-	5.068	-0.043

(D) DIHEDRAL ANGLES

PLANE A	PLANE B	∠ AB
1	2	1.8°
1	3	0.7
1	4	74.9
2	3	1.2
2	4	73.5
3	4	74.3

3.3 Discussion

Although the analyses described in Part II of this thesis were undertaken primarily to determine first the structure of the clathrates formed by Dianin's compound and its thia-analogue and secondly the orientation of guest molecules within the cavity of the clathrate, the results obtained allow something to be said concerning the relative conformations of the host molecules, 4-p-hydroxyphenyl-2,2,4-trimethylchroman and 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman.

The chroman ring of 4-p-hydroxyphenyl-2,2,4-trimethylchroman adopts a slightly flattened half-chair conformation, the atom C(2) being displaced approximately 0.15 Å less than C(3) from the mean plane through the chroman residue. This may be compared with the di-hydroxyflavanone, Obtusifolin, (Hoppe et al., 1971), in which only the atom adjacent to the oxide group is displaced significantly from the mean plane through the flavanone residue.

The six-membered heterocyclic ring of 4-p-hydroxyphenyl-2,2,4-trimethylthiachroman adopts the classical half-chair conformation in which the atoms on the side opposite to the benzene ring are normally staggered as in cyclohexene, C(2) and C(3) being equally displaced on either side of the mean plane through the thiachroman residue. This compares favourably with the analysis of 2,2-dimethylthiachromanone-1,1-dioxide (Hoppe et al., 1969; Preuss et al., 1971) in which one of the two conformations present

is equivalent to that adopted by the thiachroman ring in 4-*p*-hydroxyphenyl-2,2,4-trimethylthiachroman.

PART III

CRYSTAL STRUCTURE ANALYSES

OF

ORGANIC COMPOUNDS

Chapter 1

The Crystal and Molecular Structure

of

2,7-Dihydro-3,6-di-p-tolyl-1,4,5-thiadiazepin-1,1-dioxide

1.1 Experimental

Crystal Data

2,7-dihydro-3,6-di-p-tolyl-1,4,5-thiadiazepine-1,1-dioxide

$C_{18}H_{18}N_2O_2S$ F.W. = 326.4

Triclinic, $\underline{a}$ = 9.44 Å, $\underline{b}$ = 12.32 Å, $\underline{c}$ = 8.21 Å,

$\alpha = 117.6^\circ, \beta = 93.7^\circ, \gamma = 104.8^\circ$

U = 799 $Å^3$ F(000) = 344 electrons

D_m = 1.35 $g.cm.^{-3}$ Z = 2 D_x = 1.357 $g.cm.^{-3}$

Space group: $P\bar{1}$ (C_i^1, No. 2)

Linear absorption coefficient (Cu K_α, λ = 1.5418 Å) = 19 $cm.^{-1}$

The crystals used in this analysis were supplied by Professor J.D. Loudon. They consisted of colourless plates. Unit cell dimensions were obtained from rotation and Weissenberg photographs (Cu K_α, radiation, λ = 1.5418 Å) taken about the $\underline{a}$, $\underline{b}$ and $\underline{c}$ axes. The space group is either P1 (No. 1) or $P\bar{1}$ (No. 2). The centrosymmetric space group ($P\bar{1}$) was chosen and this choice has been justified by the success of the subsequent analysis.

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the 0kl,...,7kl reciprocal lattice nets taken with Cu K_α radiation. The multiple film technique of Robertson, (1943) was used. The observed intensities were reduced to structure amplitudes by applying the

appropriate Lorentz, polarisation and rotation factors (Tunell, 1939). 2555 independent structure amplitudes (Table 1.4) were obtained, which represents 70 % of the data accessible to Cu K_α radiation. No absorption corrections were applied to the data.

The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

1.2 Solution and Refinement of the Structure

In the space group $P\bar{1}$, the equivalent positions are:-

$$\pm (x, y, z).$$

Therefore a heavy atom in a general position will give rise to a single set of vectors:-

$$\pm (2x, 2y, 2z).$$

The asymmetric unit of the three-dimensional Patterson summation was calculated and interpreted. The largest peak present was chosen as the heavy atom vector. The values obtained for the coordinates of the sulphur atom were:-

ATOM	X/a	Y/b	Z/c
S(1)	0.4249	0.2015	0.1806

A set of structure factors, based on the coordinates of the sulphur, was calculated and the calculated phase angles used in conjunction with the observed structure amplitudes to evaluate an electron density synthesis. The coordinates of all the remaining non-hydrogen atoms in the structure were obtained from this initial electron density synthesis. The different chemical species present in the structure were differentiated on the basis of peak height and knowledge of the chemical structure.

Inclusion of the remaining twenty-two atoms (2 oxygen, 2 nitrogen and 18 carbon) in the structure factor calculation reduced the residual, R, from 0.57 to 0.277. Two further cycles of

Fourier refinement reduced the R-factor to 0.200.

The structure was then refined in eight cycles of least-squares minimisation of the function $M = \sum w(|F_o| - |F_c|)^2$. D.R. Pollard's least-squares program, (1968) was used in the initial stages of the refinement. The parameters refined were three positional and one isotropic thermal parameter for each atom and an individual scale factor for each reciprocal lattice net. Three consecutive cycles of refinement, in which the observations were given unit weight and the full matrix of the normal equations was evaluated, reduced the residual, R, to 0.157. A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 5/|F_o|_{max}$ was then applied and a further cycle of least-squares refinement reduced the R-factor to 0.155.

On the assumption that the data were now on the same relative scale, the isotropic thermal parameters were replaced by six anisotropic temperature factors and the individual layer scale factors by one overall scale factor. The refinement was continued using the Glasgow S.F.L.S. program (Cruickshank and Smith, 1965). Convergence was achieved in a further four cycles of refinement in which the block diagonal approximation to the matrix of the normal equations was used. The R-factor at the conclusion of the analysis

was 0.122. The weighting scheme used in the last four cycles of refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$$

where $p_1 = 5$, $p_2 = 0.01$ and $p_3 = 0.001$ respectively.

In the final cycle of refinement, the shifts in both positional and thermal parameters were not significant, being less than one fifth of the corresponding standard deviations. The atomic scattering factors used throughout this analysis were those of Hoerni and Ibers, (1954) for carbon, nitrogen and oxygen and those of Dawson, (1960) for sulphur. The course of the analysis is summarised in Table 1.1.

Tables 1.2 and 1.3 contain the final values of the fractional atomic coordinates and anisotropic temperature factors together with their estimated standard deviations. The observed and final calculated structure amplitudes are listed in Table 1.4. Atomic coordinates in Angstroms referred to orthogonal axes defined by X' parallel to $\underline{a}^*$, Y' normal to $\underline{a}^*$ and $\underline{c}$ and Z' parallel to $\underline{c}$ are given in Table 1.5. Tables 1.6 and 1.7 contain the bond lengths and interbond angles in the structure together with their estimated standard deviations. Table 1.8 lists all intermolecular contacts between atoms which are less than 4 Å. In Table 1.9 the equations of the mean planes through portions of the molecule are given, together with the deviations of certain atoms from these planes.

Estimated standard deviations, where quoted, are in units of the last decimal place of the quantity to which they refer.

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 1.1. The thiadiazepine residue projected along a line in the mean planes through C(2), C(3), N(4), N(5) and C(17); and through N(4), N(5), C(6), C(7) and C(10) is shown in Figs. 1.2 and 1.3 respectively. The thiadiazepine residue projected along a line through N(4) and N(5) is shown in Fig. 1.4. The general packing of the molecules in the unit cell, as projected on (100), is illustrated in Fig. 1.5.

TABLES AND DIAGRAMS

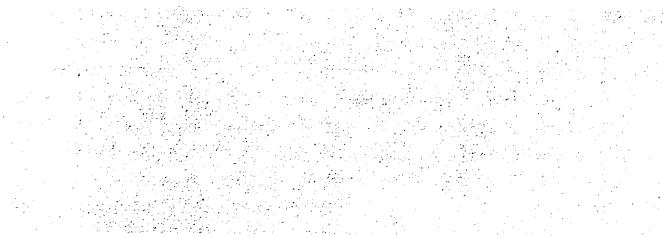
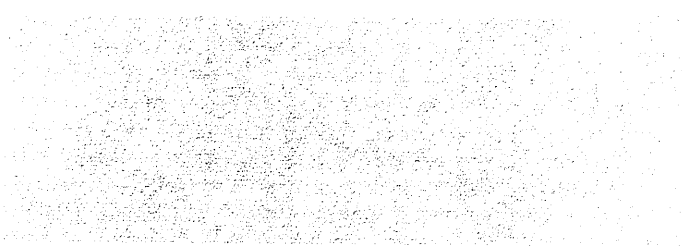


FIGURE 1.1

A molecular drawing illustrating the numbering of the non-hydrogen atoms of the molecule.



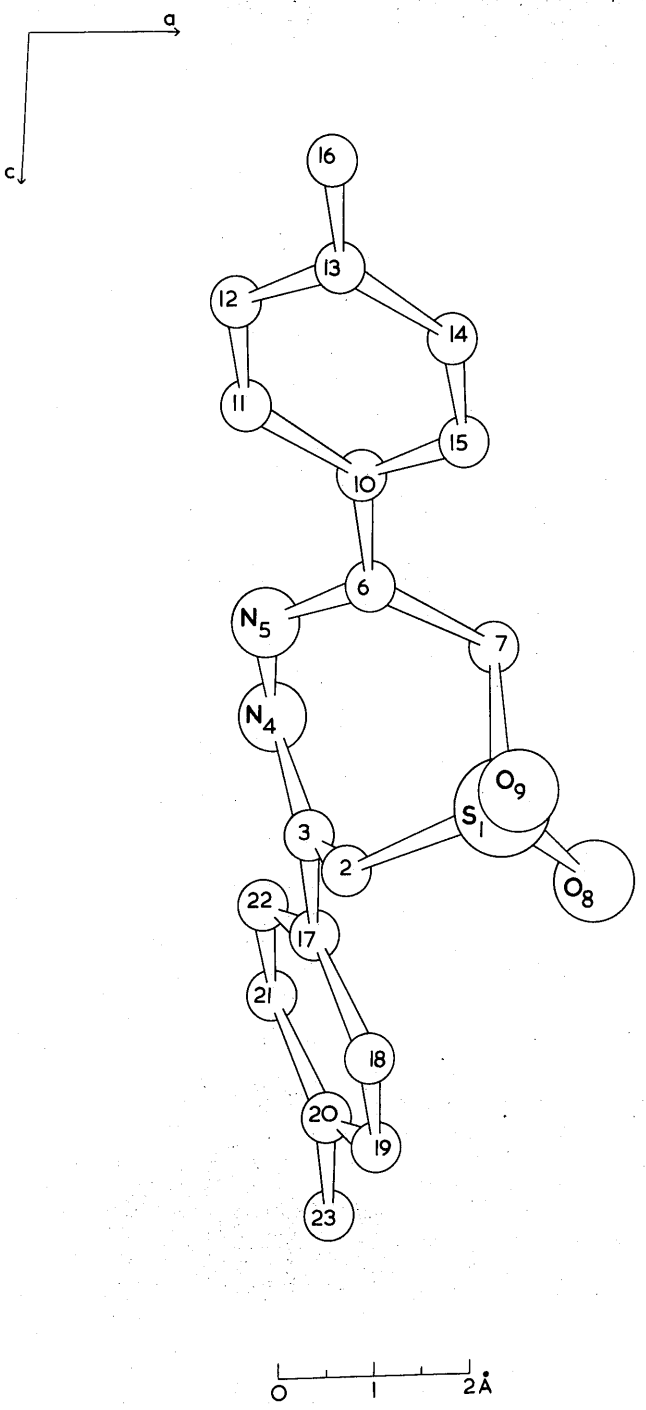

a
c
16
13
12
14
11
15
10
6
N5
7
N4
O9
S1
3
2
O8
22
17
21
18
20
19
23
0
1
2Å

FIGURE 1.2

A molecular drawing illustrating the thiadiazepine residue projected along a line in the mean molecular plane through C(2), C(3), N(4), N(5) and C(17).

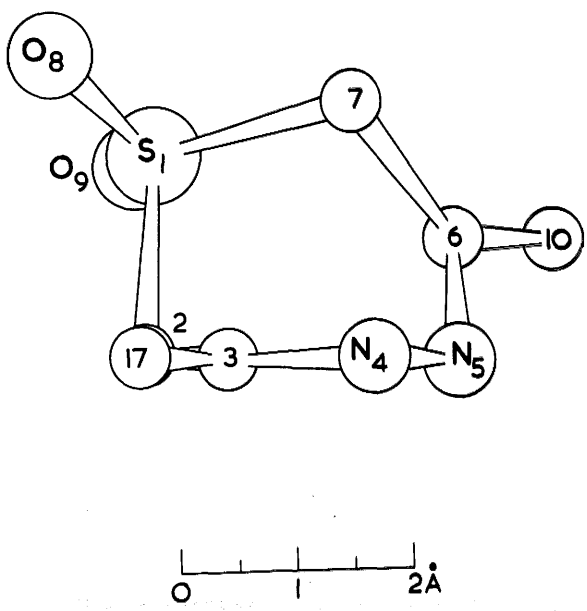

O8
O9
S1
7
6
10
2
17
3
N4
N5
0
1
2Å

FIGURE 1.3

A molecular drawing illustrating the thiadiazepine residue projected along a line in the mean molecular plane through N(4), N(5), C(6), C(7) and C(10).

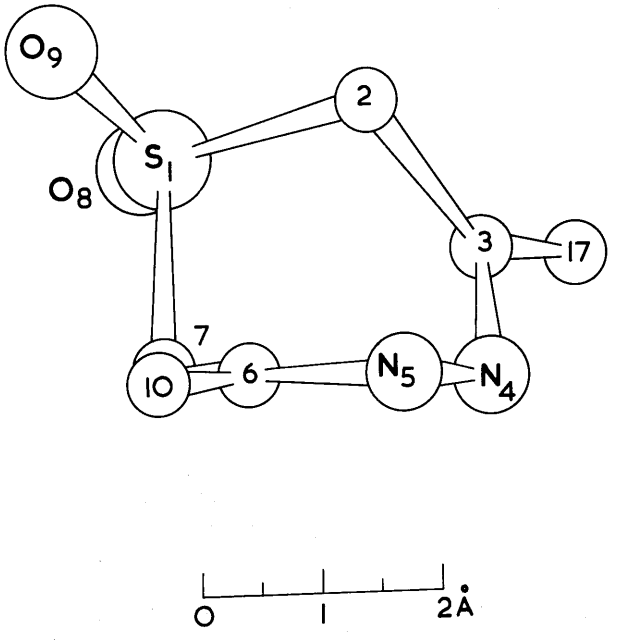

O9
2
S1
O8
3
17
7
10
6
N5
N4
0
1
2Å

FIGURE 1.4

A molecular drawing illustrating the thiadiazepine residue projected along a line through N(4) and N(5).

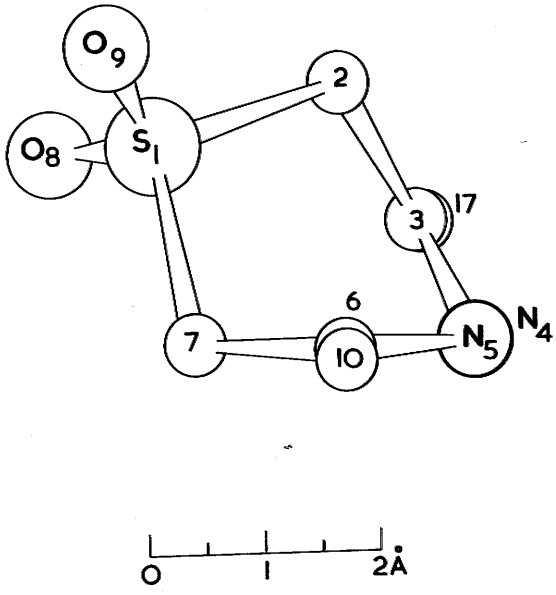

O9
2
O8
S1
17
3
6
7
10
N5
N4
0
1
2Å

FIGURE 1.5

The packing of the molecules as projected on (100).

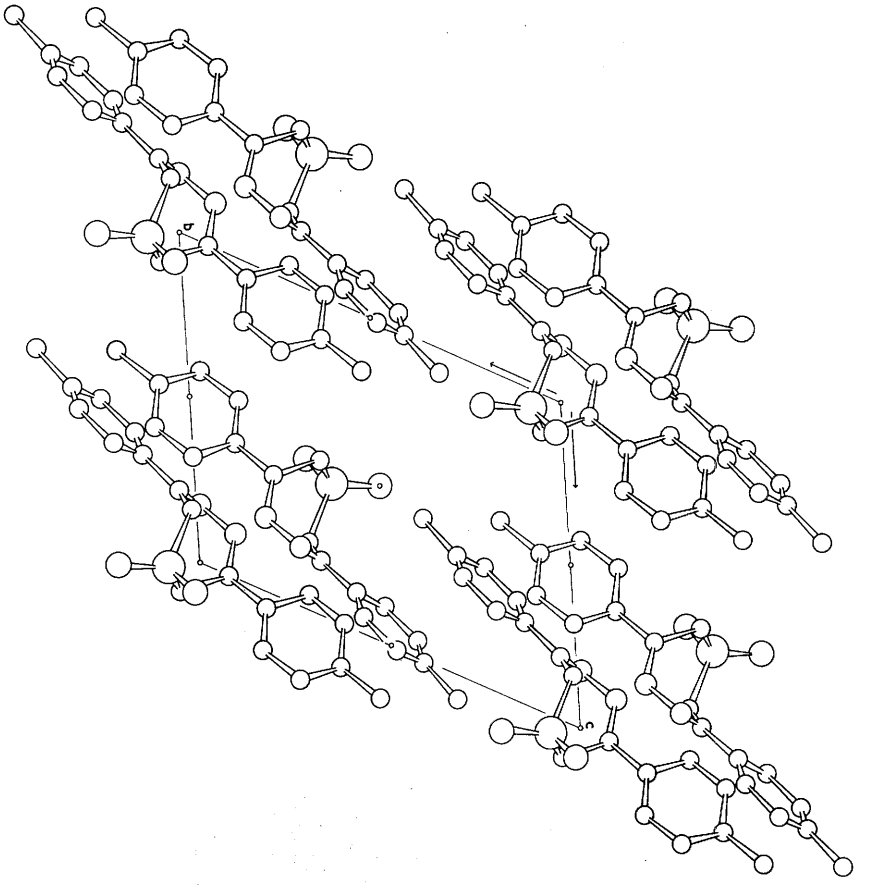


TABLE 1.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	S	0.57
2	S + 18 C + 2 N + 2 O	0.277
3	S + 18 C + 2 N + 2 O	0.204
4	S + 18 C + 2 N + 2 O	0.200

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layer scales, unit weights	0.161
2	"	0.158
3	"	0.157
4	As above, weighting scheme 1 applied	0.155
5	Block diagonal, individual anisotropic temperature factors, overall scale factor, weighting scheme 2 applied	0.128
6	"	0.124
7	"	0.123
8	"	0.122

TABLE 1.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
S(1)	0.4255 ± 2	0.2022 ± 1	1.1802 ± 2
C(2)	0.2465 ± 8	0.1239 ± 6	1.1998 ± 9
C(3)	0.1979 ± 8	-0.0179 ± 5	1.0561 ± 8
N(4)	0.1499 ± 7	-0.0583 ± 5	0.8811 ± 8
N(5)	0.1349 ± 7	0.0287 ± 5	0.8252 ± 8
C(6)	0.2545 ± 8	0.1140 ± 5	0.8408 ± 8
C(7)	0.4045 ± 9	0.1257 ± 6	0.9289 ± 9
O(8)	0.5355 ± 7	0.1666 ± 6	1.2548 ± 8
O(9)	0.4426 ± 7	0.3365 ± 4	1.2542 ± 8
C(10)	0.2377 ± 8	0.2015 ± 5	0.7671 ± 8
C(11)	0.0992 ± 8	0.1784 ± 7	0.6619 ± 10
C(12)	0.0818 ± 9	0.2579 ± 7	0.5902 ± 9
C(13)	0.2015 ± 8	0.3623 ± 6	0.6233 ± 9
C(14)	0.3365 ± 9	0.3864 ± 6	0.7284 ± 11
C(15)	0.3557 ± 9	0.3075 ± 7	0.8013 ± 11
C(16)	0.1849 ± 11	0.4448 ± 7	0.5371 ± 11
C(17)	0.2112 ± 8	-0.1128 ± 5	1.1144 ± 8
C(18)	0.2846 ± 8	-0.0765 ± 6	1.2938 ± 9
C(19)	0.2972 ± 9	-0.1683 ± 7	1.3416 ± 10
C(20)	0.2374 ± 9	-0.2986 ± 7	1.2123 ± 10

C(21)	0.1653 ± 11	-0.3350 ± 7	1.0329 ± 11
C(22)	0.1506 ± 9	-0.2452 ± 6	0.9829 ± 9
C(23)	0.2461 ± 12	-0.3987 ± 9	1.2661 ± 14

TABLE 1.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
S(1)	0.0326 10	0.0327 6	0.0450 7	0.0363 11	0.0011 12	0.0084 11
C(2)	0.0371 45	0.0341 26	0.0461 30	0.0312 46	0.0231 52	0.0272 48
C(3)	0.0296 41	0.0346 25	0.0444 29	0.0418 45	0.0189 47	0.0211 45
N(4)	0.0418 38	0.0378 24	0.0467 27	0.0483 43	0.0010 45	0.0165 43
N(5)	0.0407 38	0.0375 24	0.0488 27	0.0505 43	-0.0021 46	0.0148 43
C(6)	0.0295 41	0.0346 25	0.0432 28	0.0402 45	0.0181 47	0.0240 45
C(7)	0.0481 51	0.0458 31	0.0500 33	0.0588 55	0.0315 58	0.0373 57
O(8)	0.0553 40	0.0637 31	0.0578 29	0.0638 51	-0.0123 49	0.0164 51
O(9)	0.0665 41	0.0272 20	0.0670 31	0.0265 41	0.0151 52	0.0062 41
C(10)	0.0353 43	0.0355 26	0.0443 29	0.0425 46	0.0108 49	0.0207 47
C(11)	0.0360 47	0.0517 34	0.0528 34	0.0640 58	0.0247 56	0.0306 56
C(12)	0.0422 49	0.0542 35	0.0488 33	0.0604 57	0.0269 57	0.0394 60
C(13)	0.0432 46	0.0365 27	0.0425 29	0.0379 46	0.0183 52	0.0358 51

C(14)	0.0445 51	0.0397 31	0.0705 44	0.0618 62	0.0011 66	0.0112 55
C(15)	0.0404 50	0.0437 32	0.0681 43	0.0649 63	-0.0146 65	0.0046 55
C(16)	0.0701 62	0.0489 35	0.0618 41	0.0692 65	0.0196 73	0.0478 70
C(17)	0.0332 42	0.0366 26	0.0425 28	0.0422 45	0.0281 48	0.0237 47
C(18)	0.0330 44	0.0483 32	0.0458 31	0.0504 53	0.0127 51	0.0191 52
C(19)	0.0328 47	0.0638 40	0.0534 36	0.0746 65	0.0118 57	0.0216 61
C(20)	0.0426 49	0.0513 34	0.0605 37	0.0771 62	0.0326 61	0.0368 59
C(21)	0.0717 62	0.0430 33	0.0552 38	0.0542 59	0.0172 70	0.0387 66
C(22)	0.0533 51	0.0394 29	0.0457 32	0.0421 50	0.0013 58	0.0207 56
C(23)	0.0821 72	0.0700 49	0.0874 58	0.1234 96	0.0373 96	0.0553 90

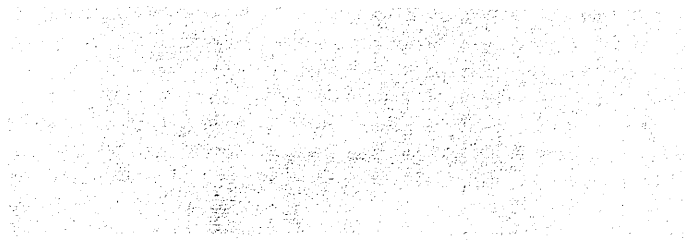
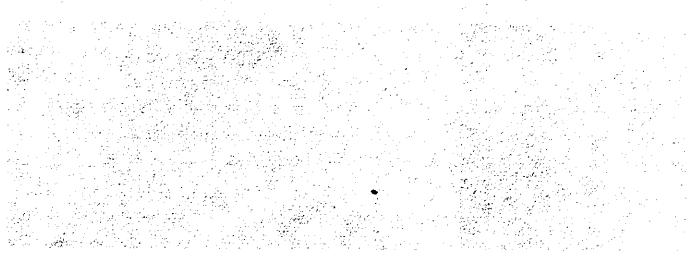


TABLE 1.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES



H	K	L	F OBS	F CALC
0	-1	0	56.2	54.3
0	-2	0	46.4	47.5
0	-3	0	13.2	6.6
0	-4	0	32.9	24.3
0	-5	0	20.6	14.8
0	-6	0	17.2	14.7
0	-7	0	8.4	9.2
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4	-15	10	2.6	2.7
4	-1	11	2.6	2.7
4	-2	11	2.6	2.7
4	-3	11	2.6	2.7
4	-4	11	2.6	2.7
4	-5	11	2.6	2.7
4	-6	11	2.6	2.7
4	-7	11	2.6	2.7
4	-8	11	2.6	2.7
4	-9	11	2.6	2.7
4	-10	11	2.6	2.7
4	-11	11	2.6	2.7
4	-12	11	2.6	2.7
4	-13	11	2.6	2.7
4	-14	11	2.6	2.7
4	-15	11	2.6	2.7
4	-1	12	2.6	2.7
4	-2	12	2.6	2.7
4	-3	12	2.6	2.7
4	-4	12	2.6	2.7
4	-5	12	2.6	2.7
4	-6	12	2.6	2.7
4	-7	12	2.6	2.7
4	-8	12	2.6	2.7
4	-9	12	2.6	2.7
4	-10	12	2.6	2.7
4	-11	12	2.6	2.7
4	-12	12	2.6	2.7
4	-13	12	2.6	2.7
4	-14	12	2.6	2.7
4	-15	12	2.6	2.7
4	-1	13	2.6	2.7
4	-2	13	2.6	2.7
4	-3	13	2.6	2.7
4	-4	13	2.6	2.7
4	-5	13	2.6	2.7
4	-6	13	2.6	2.7
4	-7	13	2.6	2.7
4	-8	13	2.6	2.7
4	-9	13	2.6	2.7
4	-10	13	2.6	2.7
4	-11	13	2.6	2.7
4	-12	13	2.6	2.7
4	-13	13	2.6	2.7
4	-14	13	2.6	2.7
4	-15	13	2.6	2.7
4	-1	14	2.6	2.7
4	-2	14	2.6	2.7
4	-3	14	2.6	2.7
4	-4	14	2.6	2.7
4	-5	14	2.6	2.7
4	-6	14	2.6	2.7
4	-7	14	2.6	2.7
4	-8	14	2.6	2.7
4	-9	14	2.6	2.7
4	-10	14	2.6	2.7
4	-11	14	2.6	2.7
4	-12	14	2.6	2.7
4	-13	14	2.6	2.7
4	-14	14	2.6	2.7
4	-15	14	2.6	2.7
4	-1	15	2.6	2.7
4	-2	15	2.6	2.7
4	-3	15	2.6	2.7
4	-4	15	2.6	2.7
4	-5	15	2.6	2.7
4	-6	15	2.6	2.7
4	-7	15	2.6	2.7
4	-8	15	2.6	2.7
4	-9	15	2.6	2.7
4	-10	15	2.6	2.7
4	-11	15	2.6	2.7
4	-12	15	2.6	2.7
4	-13	15	2.6	2.7
4	-14	15	2.6	2.7
4	-15	15	2.6	2.7
4	-1	16	2.6	2.7
4	-2	16	2.6	2.7
4	-3	16	2.6	2.7
4	-4	16	2.6	2.7
4	-5	16	2.6	2.7
4	-6	16	2.6	2.7
4	-7	16	2.6	2.7
4	-8	16	2.6	2.7
4	-9	16	2.6	2.7
4	-10	16	2.6	2.7
4	-11	16	2.6	2.7
4	-12	16	2.6	2.7
4	-13	16	2.6	2.7
4	-14	16	2.6	2.7
4	-15	16	2.6	2.7
4	-1	17	2.6	2.7
4	-2	17	2.6	2.7
4	-3	17	2.6	2.7
4	-4	17	2.6	2.7
4	-5	17	2.6	2.7
4	-6	17	2.6	2.7
4	-7	17	2.6	2.7
4	-8	17	2.6	2.7
4	-9	17	2.6	2.7
4	-10	17	2.6	2.7
4	-11	17	2.6	2.7
4	-12	17	2.6	2.7
4	-13	17	2.6	2.7
4	-14	17	2.6	2.7
4	-15	17	2.6	2.7
4	-1	18	2.6	2.7
4	-2	18	2.6	2.7
4	-3	18	2.6	2.7
4	-4	18	2.6	2.7
4	-5	18	2.6	2.7
4	-6	18	2.6	2.7
4	-7	18	2.6	2.7
4	-8	18	2.6	2.7
4	-9	18	2.6	2.7
4	-10	18	2.6	2.7
4	-11	18	2.6	2.7
4	-12	18	2.6	2.7
4	-13	18	2.6	2.7
4	-14	18	2.6	2.7
4	-15	18	2.6	2.7
4	-1	19	2.6	2.7
4	-2	19	2.6	2.7
4	-3	19	2.6	2.7
4	-4	19	2.6	2.7
4	-5	19	2.6	2.7
4	-6	19	2.6	2.7
4	-7	19	2.6	2.7
4	-8	19	2.6	2.7
4	-9	19	2.6	2.7
4	-10	19	2.6	2.7
4	-11	19	2.6	2.7
4	-12	19	2.6	2.7
4	-13	19	2.6	2.7
4	-14	19	2.6	2.7
4	-15	19	2.6	2.7
4	-1	20	2.6	2.7
4	-2	20	2.6	2.7
4	-3	20	2.6	2.7
4	-4	20	2.6	2.7
4	-5	20	2.6	2.7
4	-6	20	2.6	2.7
4	-7	20	2.6	2.7
4	-8	20	2.6	2.7
4	-9	20	2.6	2.7
4	-10	20	2.6	2.7
4	-11	20	2.6	2.7
4	-12	20	2.6	2.7
4	-13	20	2.6	2.7
4	-14	20	2.6	2.7
4	-15	20	2.6	2.7

H	K	L	F OBS	F CALC
5	-5	2	3.5	0.9
5	-6	2	12.5	12.5
5	-7	2	11.3	12.6
5	-8	2	15.9	18.0
5	-9	2	2.1	2.6
5	-10	2	12.2	12.1
5	-11	2	2.2	3.1
5	-12	2	2.2	2.2
5	-13	2	4.3	3.9
5	-14	2	3.5	2.6
5	-15	2	1.6	2.2
5	0	3	6.7	5.9
5	-1	3	20.7	21.0
5	-2	3	11.0	8.6
5	-3	3	14.8	15.0
5	-4	3	1.8	3.8
5	-5	3	7.0	5.5
5	-6	3	8.9	10.3
5	-7	3	12.9	12.7
5	-8	3	29.0	32.3
5	-9	3	9.5	8.9
5	-10	3	4.8	4.0
5	-11	3	17.5	18.5
5	-12	3	3.5	3.0
5	-13	3	9.5	9.4
5	-14	3	5.0	5.0
5	0	4	8.2	8.4
5	-1	4	7.5	6.1
5	-2	4	14.8	15.2
5	-3	4	3.8	3.8
5	-4	4	14.5	14.8
5	-5	4	2.3	1.2
5	-6	4	3.4	3.5
5	-7	4	8.2	9.3
5	-8	4	23.2	22.7
5	-9	4	5.6	5.6
5	-10	4	1.7	1.5
5	-11	4	12.4	14.7
5	-12	4	3.2	3.3
5	-14	4	4.2	4.0
5	-15	4	1.5	1.6
5	0	5	9.1	9.0
5	-1	5	5.9	6.6
5	-2	5	10.6	11.1
5	-3	5	12.1	9.1
5	-4	5	2.6	1.3
5	-5	5	13.8	12.8
5	-6	5	15.0	13.7
5	-7	5	30.0	35.7
5	-8	5	28.6	29.9
5	-9	5	2.0	1.2
5	-10	5	3.4	3.1
5	-11	5	3.4	2.7
5	-12	5	4.0	3.9
5	-13	5	2.8	2.8
5	-14	5	1.8	1.5
5	-15	5	2.0	2.1
5	-1	6	3.1	2.4
5	-2	6	8.2	8.0
5	-3	6	3.0	2.0
5	-4	6	16.4	14.3
5	-5	6	3.0	2.0
5	-6	6	8.4	7.7
5	-7	6	13.9	13.8
5	-8	6	4.9	5.9
5	-9	6	8.8	8.7
5	-10	6	4.1	3.4
5	-11	6	6.0	5.8
5	-12	6	2.8	2.7
5	-14	6	1.2	1.5
5	-15	6	1.7	1.5
5	0	7	6.2	7.3
5	-1	7	2.4	2.5
5	-2	7	7.6	8.1
5	-4	7	7.8	7.1
5	-5	7	8.0	7.2
5	-6	7	2.0	1.7
5	-7	7	5.3	4.7
5	-8	7	2.3	1.5
5	-9	7	7.6	7.5
5	-10	7	4.7	5.2
5	-11	7	3.9	3.3
5	-12	7	2.1	2.0
5	-13	7	2.8	2.6
5	-14	7	4.8	4.7
5	-15	7	5.2	4.5
5	-4	8	3.4	2.6
5	-5	8	2.1	2.0
5	-6	8	2.3	2.1
5	-7	8	2.1	2.0
5	-9	8	1.6	1.3
5	-10	8	2.5	2.5
5	-12	8	1.1	1.2
5	-13	8	4.3	3.3
5	-9	9	5.4	5.1
5	-10	9	2.6	2.5
5	-11	9	1.9	1.9
5	1	0	19.5	19.3
5	2	0	19.8	15.8
5	3	0	11.6	10.1
5	4	0	4.3	4.0
5	5	0	4.3	4.0
5	6	0	4.4	3.7
5	7	0	4.4	3.6
5	8	0	11.3	10.8
5	9	0	10.1	9.3
5	10	0	1.1	0.9
5	1	1	5.9	5.7
5	2	1	18.1	17.1
5	3	1	14.0	12.6
5	4	1	10.3	9.7
5	5	1	4.4	3.3
5	6	1	10.6	9.2
5	8	1	7.8	8.1
5	9	1	2.6	2.5
5	1	2	25.6	26.4
5	2	2	4.5	3.5
5	3	2	13.9	11.4
5	5	2	9.0	8.4
5	6	2	4.0	4.3
5	7	2	4.7	5.3
5	8	2	2.3	2.3
5	2	3	17.5	16.9
5	3	3	25.2	25.7
5	4	3	8.2	8.0
5	5	3	6.2	6.0
5	6	3	3.1	1.5
5	7	3	1.5	1.6
5	1	4	7.6	7.2
5	2	4	3.1	2.7
5	3	4	4.4	4.4
5	4	4	6.1	7.0
5	5	4	4.4	3.9
5	2	5	4.3	4.3
5	3	5	3.4	3.8
5	4	5	3.4	3.6
5	1	6	7.2	6.4
5	2	6	3.9	4.6
5	1	-1	11.3	12.8
5	2	-1	4.1	4.8
5	3	-1	1.0	0.4
5	4	-1	0.8	4.4
5	5	-1	4.2	4.5

H	K	L	F OBS	F CALC
5	6	-1	9.9	8.9
5	7	-1	1.4	0.5
5	8	-1	2.3	2.3
5	9	-1	1.3	1.3
5	10	-1	4.2	3.2
5	0	-2	29.3	27.1
5	1	-2	8.1	6.1
5	2	-2	6.8	6.4
5	3	-2	3.8	4.5
5	4	-2	10.6	9.9
5	5	-2	1.8	0.7
5	6	-2	13.9	13.0
5	7	-2	6.7	7.2
5	8	-2	17.7	16.9
5	9	-2	7.7	7.1
5	10	-2	2.1	2.1
5	11	-2	3.7	3.8
5	0	-3	32.1	26.8
5	1	-3	7.1	6.3
5	2	-3	35.3	30.7
5	3	-3	4.8	2.6
5	4	-3	10.7	9.7
5	5	-3	3.2	2.8
5	6	-3	4.4	3.9
5	7	-3	2.7	1.3
5	8	-3	5.3	4.8
5	10	-3	13.8	12.7
5	11	-3	2.2	2.1
5	0	-4	11.9	11.5
5	1	-4	3.1	2.4
5	2	-4	8.0	10.7
5	3	-4	3.6	3.5
5	4	-4	0.7	1.0
5	5	-4	2.4	1.8
5	6	-4	27.3	27.0
5	7	-4	21.5	18.8
5	8	-4	8.6	7.2
5	4	-5	15.2	14.8
5	5	-5	2.8	2.6
5	6	-5	8.3	8.8
5	7	-5	6.7	7.1
5	8	-5	2.4	1.9
5	11	-5	4.2	4.0
5	12	-5	4.4	4.6
5	0	-6	2.4	1.8
5	1	-6	8.3	7.8
5	2	-6	12.9	11.2
5	3	-6	7.0	5.7
5	4	-6	10.0	7.9
5	5	-6	7.5	4.7
5	6	-6	4.4	4.0
5	7	-6	4.4	3.6
5	8	-6	1.3	1.1
5	9	-6	4.9	4.2
5	10	-6	6.3	6.6
5	11	-6	4.6	3.7
5	12	-6	2.2	2.6
5	1	-7	6.1	6.1
5	2	-7	3.1	2.2
5	3	-7	6.4	7.1
5	4	-7	4.1	3.7
5	5	-7	3.0	2.0
5	6	-7	15.5	12.3
5	8	-7	8.1	8.9
5	9	-7	2.6	2.4
5	3	-8	2.6	1.8
5	4	-8	5.4	5.1
5	5	-8	4.2	3.5
5	6	-8	5.5	3.9
5	7	-8	13.7	10.9
5	8	-8	2.8	2.5
5	9	-8	5.9	5.0
5	10	-8	0.7	0.1
5	11	-8	4.7	4.8
5	0	-9	3.1	4.1
5	1	-9	3.1	3.2
5	2	-9	3.3	3.2
5	3	-9	2.3	2.2
5	4	-9	1.3	0.6
5	5	-9	8.9	8.7
5	6	-9	13.4	12.5
5	7	-9	1.7	1.2
5	-1	-1	18.7	17.1
5	-2	-1	15.9	13.7
5	-3	-1	27.4	20.2
5	-4	-1	7.9	4.3
5	-5	-1	1.8	1.1
5	-6	-1	3.4	2.8
5	-7	-1	9.9	7.4
5	-8	-1	1.7	1.9
5	-9	-1	9.1	7.2
5	-10	-1	14.3	11.9
5	-11	-1	4.4	4.7
5	-12	-1	3.3	3.4
5	-13	-1	3.2	3.7
5	-1	-2	31.1	27.9
5	-2	-2	10.9	10.5
5	-3	-2	9.8	6.5
5	-4	-2	18.0	16.1
5	-5	-2	5.1	4.1
5	-6	-2	11.8	8.8
5	-7	-2	12.6	11.4
5	-8	-2	13.1	12.0
5	-9	-2	3.8	2.5
5	-10	-2	5.0	4.7
5	-11	-2	3.7	4.2
5	-1	-3	3.6	3.2
5	-3	-3	4.0	2.4
5	-4	-3	14.0	12.6
5	-5	-3	16.6	17.0
5	-6	-3	7.0	4.8
5	-7	-3	3.7	3.5
5	-8	-3	7.4	5.7
5	-9	-3	2.3	1.0
5	-4	-4	3.0	3.2
5	-5	-4	2.8	2.5
5	-7	-4	3.3	2.9
5	-8	-4	2.3	1.9
5	-10	-4	2.5	3.2
5	-1	-5	10.1	8.9
5	-2	-5	12.0	10.6
5	-4	-5	18.4	16.8

H	K	L	F OBS	F CALC
6	3	1	12.4	9.9
6	4	1	3.3	2.6
6	5	1	4.6	4.2
6	6	1	7.3	7.1
6	8	1	4.7	4.9
6	1	2	5.9	3.4
6	2	2	8.9	7.5
6	3	2	15.9	15.1
6	4	2	3.0	2.1
6	5	2	4.8	4.2
6	6	2	6.3	5.5
6	7	2	0.9	0.6
6	1	3	11.1	10.9
6	2	3	17.2	16.7
6	3	3	11.0	10.1
6	5	3	4.7	5.3
6	1	4	8.6	8.3
6	2	4	11.2	9.8
6	3	4	1.6	1.7
6	4	4	5.5	5.4
6	5	4	6.0	5.5
6	6	4	5.0	5.0
6	7	4	9.4	9.8
6	1	5	1.1	1.0
6	2	5	5.0	5.0
6	3	5	9.4	9.8
6	4	5	1.4	1.4
6	5	5	4.2	3.9
6	1	6	1.1	1.0
6	2	6	7.6	7.6
6	3	6	5.3	4.6
6	4	6	2.9	2.7
6	1	-1	10.2	13.1
6	2	-1	11.7	8.0
6	3	-1	15.4	14.8
6	4	-1	14.4	12.8
6	5	-1	1.7	0.8
6	6	-1	6.9	6.8
6	7	-1	4.7	4.4
6	8	-1	8.3	7.7
6	9	-1	2.0	1.8
6	2	-2	37.2	34.1
6	3	-2	6.3	5.5
6	4	-2	13.6	14.9
6	5	-2	9.1	7.0
6	6	-2	2.8	2.5
6	7	-2	9.1	9.3
6	8	-2	2.8	2.5
6	9	-2	7.5	7.6
6	10	-2	1.9	2.0
6	3	-3	19.2	19.6
6	4	-3	7.0	6.9
6	5	-3	9.7	10.7
6	6	-3	1.6	2.9
6	7	-3	4.2	3.5
6	8	-3	4.4	4.4
6	9	-3	9.5	9.0
6	10	-3	1.3	1.5
6	11	-3	2.2	1.1
6	0	-4	5.2	4.4
6	1	-4	3.3	3.1
6	2	-4	7.2	6.2
6	3	-4	7.4	6.5
6	4	-4	11.9	11.6
6	5	-4	3.6	3.6
6	6	-4	7.0	7.6
6	7	-4	2.4	2.2
6	8	-4	1.9	1.2
6	9	-4	1.6	1.2
6	10	-4	3.9	3.8
6	11	-4	3.3	3.3
6	0	-5	8.6	8.9
6	1	-5	11.9	10.1
6	2	-5	2.0	1.6
6	3	-5	7.8	7.6
6	4	-5	6.8	7.0
6	5	-5	11.2	12.0
6	6	-5	8.0	8.2
6	7	-5	4.6	4.5
6	8	-5	4.4	4.4
6	9	-5	6.6	5.5
6	10	-5	4.3	4.9
6	11	-5	3.3	3.4
6	0	-6	4.0	3.8
6	1	-6	4.0	3.8
6	2	-6	4.4	3.7
6	3	-6	6.4	5.4
6	5	-6	3.7	2.7
6	6	-6	3.7	3.5
6	7	-6	6.2	6.2
6	8	-6	5.9	5.9
6	10	-6	7.3	8.0
6	0	-7	2.0	1.6
6	1	-7	5.3	5.6
6	2	-7	4.5	3.9
6	3	-7	6.6	6.1
6	4	-7	3.9	3.3
6	5	-7	5.8	4.6
6	6	-7	3.7	3.2
6	7	-7	4.9	4.7
6	8	-7	2.9	2.9
6	9	-7	3.1	3.1
6	10	-7	1.3	1.6
6	0	-8	4.4	4.5
6	2	-8	2.3	2.0
6	3	-8	2.1	1.4
6	4	-8	2.9	3.2
6	5	-8	3.6	3.8
6	6	-8	10.4	8.8
6	7	-8	9.4	8.2
6	8	-8	1.8	1.6
6	9	-8	3.0	2.4
6	1	-9	2.8	2.6
6	2	-9	1.0	1.5
6	3	-9	3.2	2.9
6	4	-9	1.9	1.7
6	5	-9	3.2	2.9
6	6	-9	2.6	3.0
6	7	-9	1.8	1.6
6	-1	-1	12.8	9.9
6	-2	-1	5.8	5.0
6	-3	-1	7.9	8.7
6	-4	-1	5.6	5.5
6	-5	-1	7.7	7.3
6	-6	-1	5.9	5.5
6	-7	-1	1.4	1.1
6	-8	-1	2.7	2.6
6	-9	-1	2.1	2.1
6	-10	-1	1.8	1.4
6	-11	-1	1.2	1.5
6	-12	-1	3.1	2.7
6	-1	-2	17.0	19.2
6	-2	-2	7.9	7.5
6	-3	-2	15.4	13.0
6	-4	-2	10.5	9.4
6	-5	-2	7.1	4.5
6	-6	-2	12.3	9.9
6	-7	-2	5.7	4.4
6	-8	-2	4.3	4.4
6	-9	-2	2.6	3.0
6	-10	-2	2.9	2.6
6	-11	-2	2.9	2.4
6	-1	-3	12.3	11.2
6	-3	-3	9.6	9.2
6	-5	-3	1.6	2.0
6	-6	-3	2.3	1.0
6	-7	-3	4.3	4.2
6	-8	-3	4.7	3.9
6	-9	-3	2.0	0.9
6	-4	-4	7.9	7.2

H	K	L	F OBS	F CALC
6	-5	-4	5.8	5.0
6	-6	-4	7.9	8.7
6	-7	-4	6.4	7.3
6	-8	-4	5.9	5.5
6	-9	-4	2.9	2.8
6	-10	-4	3.8	3.5
6	-11	-4	3.2	3.2
6	-12	-4	4.0	3.7
6	-13	-4	3.7	3.9
6	-14	-4	8.7	8.1
6	-6	-5	6.9	7.8
6	-5	-6	3.8	3.9
6	-6	-6	1.8	1.7
6	-7	-6	5.5	5.3
6	-2	-7	1.7	1.9
6	-4	-7	1.4	1.1
6	-5	-7	4.1	4.7
6	-6	-7	2.5	2.7
6	-2	-8	2.9	2.9
6	-4	-8	2.7	2.9
6	-5	-8	6.1	9.6
6	-1	0	10.4	13.0
6	-2	0	2.7	2.2
6	-3	0	16.2	14.6
6	-4	0	11.9	10.6
6	-5	0	2.5	1.2
6	-6	0	6.8	4.9
6	-7	0	11.0	9.7
6	-8	0	4.2	3.5
6	-9	0	1.8	1.4
6	-10	0	2.7	2.3
6	-11	0	3.9	3.8
6	-12	0	3.5	3.0
6	-13	0	4.1	4.0
6	-1	1	13.5	10.2
6	-2	1	3.5	3.5
6	-3	1	13.6	12.4
6	-4	1	3.6	3.5
6	-5	1	14.8	15.9
6	-6	1	8.5	8.1
6	-7	1	21.1	22.0
6	-10	1	2.7	2.4
6	-11	1	2.7	2.5
6	-12	1	6.4	5.0
6	-13	1	1.2	1.0
6	-14	1	4.8	4.4
6	-1	2	13.5	11.2
6	-3	2	10.9	9.2
6	-5	2	10.5	8.4
6	-7	2	13.7	14.2
6	-8	2	6.3	7.7
6	-9	2	7.6	7.6
6	-10	2	3.3	3.0
6	-11	2	3.0	2.4
6	-12	2	12.7	9.6
6	-13	2	3.7	3.0
6	-14	2	1.4	1.4
6	-1	3	4.9	4.4
6	-2	3	14.1	13.1
6	-3	3	8.1	8.0
6	-4	3	13.9	15.1
6	-5	3	9.0	7.5
6	-6	3	12.0	11.7
6	-7	3	13.9	12.4
6	-8	3	19.3	19.8
6	-9	3	12.5	11.9
6	-11	3	2.6	2.2
6	-12	3	5.3	5.3
6	-13	3	1.7	1.7
6	-14	3	4.7	3.7
6	-1	4	4.6	4.3
6	-2	4	12.8	11.4
6	-3	4	1.6	1.7
6	-4	4	5.5	5.4
6	-5	4	6.9	7.8
6	-6	4	1.8	1.7
6	-7	4	11.9	10.6
6	-8	4	2.5	1.2
6	-9	4	4.9	5.1
6	-10	4	3.5	3.4
6	-11	4	2.7	2.9
6	-12	4	3.3	2.5
6	-13	4	2.3	2.1
6	-14	4	3.7	3.7
6	-1	5	3.4	3.1
6	-2	5	2.3	2.1
6	-3	5	3.3	3.1
6	-4	5	2.3	2.1
6	-5	5	2.3	2.1
6	-6	5	2.3	2.1
6	-7	5	2.3	2.1
6	-8	5	2.3	2.1
6	-9	5	2.3	2.1
6	-10	5	2.3	2.1
6	-11	5	2.3	2.1
6	-12	5	2.3	2.1
6	-13	5	2.3	2.1
6	-14	5	2.3	2.1
6	-1	6	2.3	2.1
6	-2	6	2.3	2.1
6	-3	6	2.3	2.1
6	-4	6	2.3	2.1
6	-5	6	2.3	2.1
6	-6	6	2.3	2.1
6	-7	6	2.3	2.1
6	-8	6	2.3	2.1
6	-9	6	2.3	2.1
6	-10	6	2.3	2.1
6	-11	6	2.3	2.1
6	-12	6	2.3	2.1
6	-13	6	2.3	2.1
6	-14	6	2.3	2.1
6	-1	7	2.3	2.1
6	-2	7	2.3	2.1
6	-3	7	2.3	2.1
6	-4	7	2.3	2.1
6	-5	7	2.3	2.1
6	-6	7	2.3	2.1
6	-7	7	2.3	2.1
6	-8	7	2.3	2.1
6	-9	7	2.3	2.1
6	-10	7	2.3	2.1
6	-11	7	2.3	2.1
6	-12	7	2.3	2.1
6	-13	7	2.3	2.1
6	-14	7	2.3	2.1
6	-1	8	2.3	2.1
6	-2	8	2.3	2.1
6	-3	8	2.3	2.1
6	-4	8	2.3	2.1
6	-5	8	2.3	2.1
6	-6	8	2.3	2.1
6	-7	8	2.3	2.1
6	-8	8	2.3	2.1
6	-9	8	2.3	2.1
6	-10	8	2.3	2.1
6	-11	8	2.3	2.1
6	-12	8	2.3	2.1
6	-13	8	2.3	2.1
6	-14	8	2.3	2.1
6	-1	9	2.3	2.1
6	-2	9	2.3	2.1
6	-3	9	2.3	2.1
6	-4	9	2.3	2.1
6	-5	9	2.3	2.1
6	-6	9	2.3	2.1
6	-7	9	2.3	2.1
6	-8	9	2.3	2.1
6	-9	9	2.3	2.1
6	-10	9	2.3	2.1
6	-11	9	2.3	2.1
6	-12	9	2.3	2.1
6	-13	9	2.3	2.1
6	-14	9	2.3	2.1
6	-1	10	2.3	2.1
6	-2	10	2.3	2.1
6	-3	10	2.3	2.1
6	-4	10	2.3	2.1
6	-5	10	2.3	2.1
6	-6	10	2.3	2.1
6	-7	10	2.3	2.1
6	-8	10	2.3	2.1
6	-9	10	2.3	2.1
6	-10	10	2.3	2.1
6	-11	10	2.3	2.1
6	-12	10	2.3	2.1
6	-13	10	2.3	2.1
6	-14	10	2.3	2.1
6	-1	11	2.3	2.1
6	-2	11	2.3	2.1
6	-3	11	2.3	2.1
6	-4	11	2.3	2.1
6	-5	11	2.3	2.1
6	-6	11	2.3	2.1
6	-7	11	2.3	2.1
6	-8	11	2.3	2.1
6	-9	11	2.3	2.1
6	-10	11	2.3	2.1
6	-11	11	2.3	2.1
6	-12	11	2.3	2.1
6	-13	11	2.3	2.1
6	-14	11	2.3	2.1

H	K	L	F OBS	F CALC
7	6	1	9.1	7.8
7	7	1	5.3	6.0
7	1	2	18.0	14.9
7	2	2	25.3	20.9
7	3	2	4.8	2.3
7	4	2	14.7	8.3
7	5	2	7.2	3.8
7	6	2	4.8	3.8
7	1	3	4.7	4.2
7	2	3	3.8	3.8
7	3	3	3.2	2.5
7	4	3	3.5	3.4
7

TABLE 1.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X'	Y'	Z'
S(1)	3.796 ± 2	0.920 ± 2	8.282 ± 2
C(2)	2.199 ± 7	0.608 ± 6	8.997 ± 7
C(3)	1.766 ± 7	-0.795 ± 6	8.656 ± 6
N(4)	1.337 ± 6	-1.090 ± 5	7.478 ± 5
N(5)	1.204 ± 6	-0.095 ± 5	6.532 ± 5
C(6)	2.270 ± 7	0.475 ± 6	6.101 ± 6
C(7)	3.609 ± 8	0.149 ± 7	6.667 ± 6
O(8)	4.777 ± 6	0.198 ± 6	9.032 ± 6
O(9)	3.949 ± 6	2.335 ± 5	8.113 ± 6
C(10)	2.121 ± 7	1.481 ± 6	5.007 ± 6
C(11)	0.885 ± 8	1.648 ± 7	4.358 ± 6
C(12)	0.730 ± 8	2.568 ± 7	3.326 ± 6
C(13)	1.798 ± 8	3.346 ± 6	2.930 ± 6
C(14)	3.003 ± 8	3.200 ± 7	3.574 ± 8
C(15)	3.174 ± 8	2.281 ± 7	4.612 ± 8
C(16)	1.650 ± 10	4.297 ± 7	1.761 ± 8
C(17)	1.884 ± 7	-1.871 ± 6	9.669 ± 6
C(18)	2.539 ± 7	-1.697 ± 7	10.891 ± 6
C(19)	2.652 ± 8	-2.736 ± 8	11.799 ± 7
C(20)	2.118 ± 8	-3.979 ± 7	11.517 ± 7

C(21)	1.474 ± 10	-4.157 ± 7	10.295 ± 8
C(22)	1.344 ± 8	-3.133 ± 7	9.380 ± 7
C(23)	2.196 ± 11	-5.098 ± 9	12.525 ± 9

TABLE 1.6

BOND LENGTHS AND E.S.D.S.

S(1) - C(2)	1.777 ± 7 Å	C(11)- C(12)	1.391 ± 10 Å
S(1) - C(7)	1.799 ± 7	C(12)- C(13)	1.379 ± 10
S(1) - O(8)	1.431 ± 6	C(13)- C(14)	1.374 ± 11
S(1) - O(9)	1.434 ± 5	C(13)- C(16)	1.514 ± 10
C(2) - C(3)	1.507 ± 8	C(14)- C(15)	1.397 ± 11
C(3) - N(4)	1.288 ± 8	C(17)- C(18)	1.397 ± 9
C(3) - C(17)	1.482 ± 8	C(17)- C(22)	1.403 ± 9
N(4) - N(5)	1.379 ± 8	C(18)- C(19)	1.385 ± 10
N(5) - C(6)	1.284 ± 9	C(19)- C(20)	1.381 ± 11
C(6) - C(7)	1.490 ± 10	C(20)- C(21)	1.393 ± 11
C(6) - C(10)	1.494 ± 8	C(20)- C(23)	1.508 ± 11
C(10)- C(11)	1.406 ± 10	C(21)- C(22)	1.380 ± 10
C(10)- C(15)	1.380 ± 10		

TABLE 1.7

INTERBOND ANGLES AND E.S.D.S.

C(2) - S(1) - C(7)	101.1 ± 3°	C(11)- C(10)- C(15)	118.0 ± 6°
C(2) - S(1) - O(8)	108.5 ± 3	C(10)- C(11)- C(12)	121.2 ± 7
C(2) - S(1) - O(9)	108.5 ± 3	C(11)- C(12)- C(13)	120.0 ± 7
C(7) - S(1) - O(8)	109.0 ± 3	C(12)- C(13)- C(14)	119.0 ± 6
C(7) - S(1) - O(9)	109.2 ± 3	C(12)- C(13)- C(16)	120.0 ± 7
O(8) - S(1) - O(9)	119.1 ± 4	C(14)- C(13)- C(16)	120.9 ± 7
S(1) - C(2) - C(3)	109.3 ± 5	C(13)- C(14)- C(15)	121.7 ± 7
C(2) - C(3) - N(4)	121.1 ± 5	C(10)- C(15)- C(14)	120.0 ± 7
C(2) - C(3) - C(17)	119.9 ± 5	C(3) - C(17)- C(18)	123.0 ± 6
N(4) - C(3) - C(17)	119.0 ± 5	C(3) - C(17)- C(22)	118.8 ± 6
C(3) - N(4) - N(5)	119.7 ± 5	C(18)- C(17)- C(22)	118.2 ± 6
N(4) - N(5) - C(6)	118.0 ± 6	C(17)- C(18)- C(19)	121.2 ± 6
N(5) - C(6) - C(7)	121.4 ± 6	C(18)- C(19)- C(20)	120.6 ± 6
N(5) - C(6) - C(10)	117.5 ± 6	C(19)- C(20)- C(21)	118.2 ± 6
C(7) - C(6) - C(10)	121.1 ± 6	C(19)- C(20)- C(23)	120.7 ± 7
S(1) - C(7) - C(6)	109.9 ± 5	C(21)- C(20)- C(23)	121.0 ± 7
C(6) - C(10)- C(11)	120.4 ± 6	C(20)- C(21)- C(22)	122.0 ± 7
C(6) - C(10)- C(15)	121.6 ± 6	C(17)- C(22)- C(21)	119.7 ± 7

TABLE 1.8

INTERMOLECULAR CONTACTS BELOW 4 Å

C(2).....C(13)	ii	3.50 Å	C(13)....C(21)	i	3.81 Å
C(2).....C(12)	ii	3.53	O(9).....C(13)	ii	3.85
N(5).....C(12)	iv	3.54	C(2).....C(16)	ii	3.86
C(16)....C(23)	iii	3.55	O(9).....C(14)	ii	3.89
O(9).....C(16)	ii	3.55	C(2).....C(14)	ii	3.89
N(4).....C(12)	iv	3.63	C(2).....C(11)	ii	3.95
N(5).....C(11)	iv	3.73	C(18)....C(10)	ii	3.96
C(16)....C(21)	i	3.75	C(16)....C(22)	i	3.99
C(11)....C(11)	iv	3.77			

Roman numerals refer to the transformations of the fractional coordinates given in Table 1.2.

i x, 1 + y, z; iii x, 1 + y, -1 + z;

ii x, y, 1 + z; iv -x, -y, 1 - z;

The transformations are applied to the coordinates of the second atom in each case.

TABLE 1.9

MEAN MOLECULAR PLANES

(A) ATOMS DEFINING PLANES

PLANE NO.	ATOMS DEFINING PLANE
1	C(6), C(10), C(11), C(12), C(13), C(14), C(15) and C(16)
2	C(3), C(17), C(18), C(19), C(20), C(21), C(22) and C(23)
3	C(2), C(3), N(4), N(5) and C(17)
4	N(4), N(5), C(6), C(7) and C(10)

(B) PLANE EQUATIONS

PLANE NO.	P	Q	R	S	RMS D
1	0.2673	-0.7021	-0.6600	-3.7837	0.024
2	0.8654	-0.2812	-0.4147	-1.8410	0.013
3	0.9291	-0.1988	-0.3119	-0.8901	0.011
4	0.1233	-0.7086	-0.6948	-4.2871	0.023

P, Q and R are the direction cosines of the plane normal, S is the plane to origin distance and RMS D is the root mean square deviation of the atoms defining the plane, from the plane, in Angstroms. The plane equation is then

$$PX + QY + RZ = S$$

where X, Y and Z are coordinates in Angstroms referred to standard orthogonal axes.

(C) DEVIATIONS FROM PLANES (Å)

PLANE NO. ATOM	1	2	3	4
S(1)	-	-	1.651	-1.651
C(2)	-	-0.159	0.006	-2.123
C(3)	-	0.002	-0.011	-0.946
N(4)	-0.029	0.202	0.017	0.028
N(5)	-0.139	0.200	-0.010	-0.035
C(6)	0.031	-	1.002	-0.008
C(7)	0.244	-	2.134	-0.006
O(8)	-	-	2.472	-1.540
O(9)	-	-	1.565	-2.517
C(10)	0.006	-	1.005	0.021
C(11)	-0.013	-	0.025	0.201
C(12)	-0.019	-	0.020	0.247
C(13)	-0.019	-	0.981	0.102
C(14)	-0.019	-	1.929	-0.093
C(15)	-0.013	-	1.947	-0.142
C(16)	0.046	-	1.020	0.223
C(17)	-	-0.013	-0.003	-0.873
C(18)	-	-0.002	0.190	-1.764
C(19)	-	0.011	0.218	-1.645
C(20)	-	0.016	0.058	-0.634

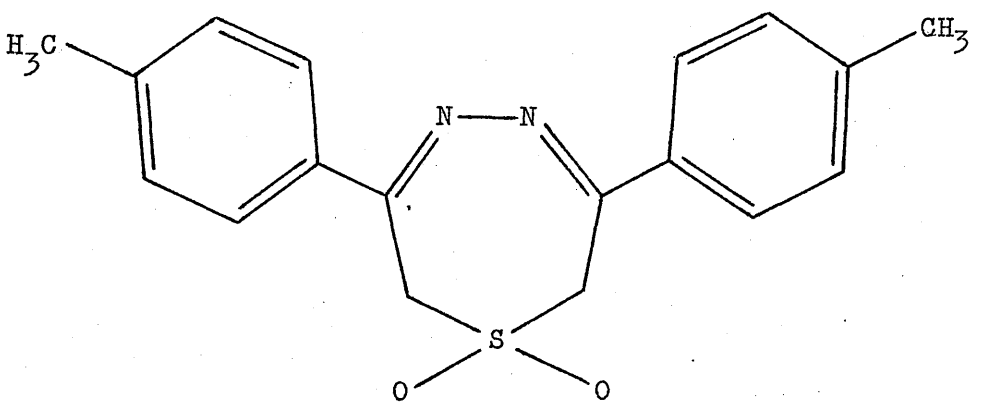
C(21)	-	0.015	-0.124	0.262
C(22)	-	-0.007	-0.164	0.155
C(23)	-	-0.021	0.038	-0.532

(D) DIHEDRAL ANGLES

PLANE A	PLANE B	∠ AB
1	2	45.4°
1	3	53.6
1	4	8.5
2	3	8.4
2	4	53.6
3	4	61.8

1.3 Discussion

The analysis was undertaken to determine the molecular dimensions and conformation of the heterocyclic unsaturated seven-membered ring in 2,7-dihydro-3,6-di-p-tolyl-1,4,5-thiadiazepine-1,1-dioxide shown below (Loudon and Young, 1963).



(I)

The two para tolyl rings are trigonally bonded to the central ring. The average value of the C-C bond distances within these rings is 1.389 ± 0.010 Å which does not differ significantly from the generally accepted value (1.395 Å) given in the literature. The average deviation of the atoms comprising the para tolyl groups from the mean planes through the rings is 0.024 Å in each case. The C(13)-C(16) and C(20)-C(23) distances of 1.508 and 1.514 Å respectively may be compared with the other $C_{sp^2} - C_{sp^3}$ distances within the central ring (1.490 and 1.507 Å) and with the value given in the literature, 1.510 Å (Sutton, 1965).

The N(4)-N(5) bond length of 1.379 Å agrees closely with the N-N single bond distance of 1.383 Å which has been found previously in a system where the nitrogen atoms in turn form double bonds with the adjacent carbon atoms (Bak et al., 1956). However the C=N double bond distances of 1.284 and 1.288 Å are considerably shorter than the values (1.302 - 1.327 Å) previously reported for such distances (Trefonas et al., 1966; 1970).

The bond lengths and angles of the sulphone group are given in Tables i and ii together with representive values taken from the literature for comparison.

Table i

(Bond Lengths)

Type	Mean Value	Literature[a]	Literature[b]
S-O	1.432 ± 0.006 Å	1.432 ± 0.005 Å	1.445 ± 0.016 Å
S-C	1.788 ± 0.007	1.765 ± 0.006	1.778 ± 0.017

Table ii

(Interbond Angles)

Type	Mean Value	Literature[a]	Literature[b]
C-S-O	108.8 ± 0.3°	107.7 ± 0.3°	108.8 ± 0.8°
C-S-C	101.1 ± 0.3	104.8 ± 0.4	103.0 ± 0.8
O-S-O	119.1 ± 0.4	120.4 ± 0.4	117.9 ± 0.8

a Sime and Abrahams, (1960); b Sands, (1963)

As in other sulphones, the bond arrangement within the sulphone is not that of a regular tetrahedron. The O-S-O bond angle is significantly greater than 109.5°, whereas the C-S-O and C-S-C angles in the present structure, as in other cases, are significantly less than tetrahedral. The deviations of the bond angles from the ideal tetrahedral value of 109.5° may be attributed to the d-orbital contributions from sulphur (Moffitt, 1950).

There has been a considerable amount of discussion in the literature on the length of the carbon-sulphur single bond in a variety of substances. The C-S bond length of approximately 1.78 Å in this and in other comparable sulphones is significantly less than the standard single bond length of 1.82 Å (Abrahams, 1956).

The S-O bond length in this, as in other sulphones, appears to be very close to 1.43 Å, the standard S=O double bond distance. The very short S-O bonds characteristic of these compounds may be indicative of π - bonding involving the 3d orbitals of sulphur (Moffitt, 1950).

Of the two possible conformations in which the C=N double bonds are (a) eclipsed, the envelope conformation and (b) skewed with respect to each other, the boat conformation, the relatively rigid conformation (b) adopted by the seven-membered heterocyclic ring and shown in Figs. 1.2, 1.3 and 1.4 respectively may be such as to minimise the repulsion between the adjacent C=N double bonds.

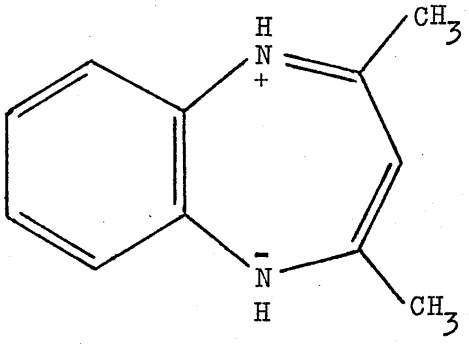
This effect may be such as to outweigh that due to conjugation between the adjacent C=N double bonds which would occur if conformation (a) were adopted. However a survey of carbocyclic seven-membered rings in sesquiterpenes indicates that the ring conformation is greatly dependent on the molecular environment (Mathieson, 1967). The dihedral angle of approximately 62° between the planes through C(2), C(3), N(4), N(5) and C(17) and through N(4), N(5), C(6), C(7) and C(10) is considerably greater than that found in 3,7-bis(p-iodophenyl)-4,5,6-triphenyl-4H-1,2-diazepine (Trefonas et al., 1970) which however contains an additional double bond within the seven-membered heterocyclic ring. Evidence from n.m.r. studies suggests that 2,7-dihydro-3,6-di-p-tolyl-1,4,5-thiadiazepine-1.1-dioxide (I) adopts a similar conformation in solution to that observed in the solid state (D.D. MacNicol, 1965).

Chapter 2

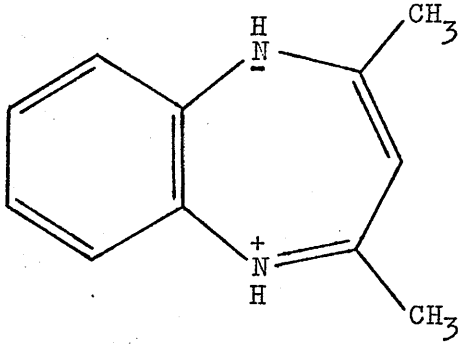
The Crystal and Molecular Structure of 2,4-Dimethyl-1,5-benzodiazepinium Bromide

2.1 Introduction

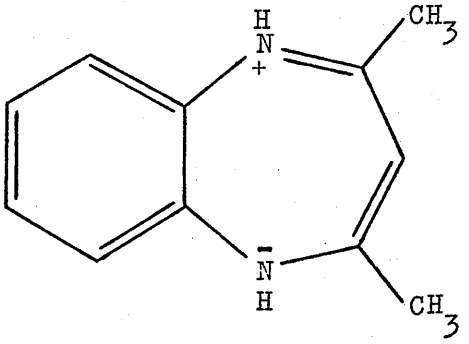
In the course of investigations into the condensation of 1,3-diketones with substituted diamines, by the method of Thiele and Steimmig, (1907), Lloyd et al., (1965) prepared a series of related benzodiazepines. Although the 3H-1,5-benzodiazepine bases have been shown to have the dianil type of structure (Finar, 1958; Barltrop et al., 1959), the mono-acid salts have intense purple colours indicating that a tautomeric shift to structure (I) has taken place during or after protonation. Thus a conjugated system, involving both rings, and given by the canonical formulae (I - IV) may be present.



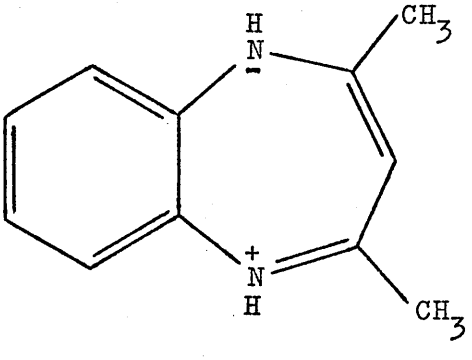
(I)



(II)



(III)



(IV)

Since the cation (I) has 12 π - electrons, it does not satisfy the requirements of Huckel's (4n + 2) rule and thus will not possess any marked aromatic character. The present analysis was undertaken in order to confirm the preceding postulations regarding the structure of 2,4-dimethyl-1,5-benzodiazepinium bromide.

2.2 Experimental

Crystal Data

2,4-dimethyl-1,5-benzodiazepinium bromide

$C_{11}H_{13}BrN_2$ F.W. = 253.2

Orthorhombic, $\underline{a}$ = 19.62 Å, $\underline{b}$ = 6.96 Å, $\underline{c}$ = 19.08 Å

U = 2605 $Å^3$ F(000) = 1024 electrons

D_m = 1.28 $g.cm.^{-3}$ Z = 8 D_x = 1.291 $g.cm.^{-3}$

Space group: Pbca (D_{2h}^{15}, No. 61)

Linear absorption coefficient (Cu K_α, λ = 1.5418 Å) = 45 $cm.^{-1}$

The crystals used in this analysis were supplied by Dr. D. Lloyd. They consisted of purple needles elongated along the $\underline{b}$-axis. Unit cell dimensions were obtained from rotation and Weissenberg photographs (Cu K_α radiation, λ = 1.5418 Å) taken about the $\underline{b}$-axis. From the systematically absent spectra, the space group was uniquely determined as Pbca (No. 61).

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the h0l,...,h6l reciprocal lattice nets taken with Cu K_α radiation. The multiple film technique of Robertson, (1943) was used. The observed intensities were reduced to structure amplitudes by applying the appropriate Lorentz, polarisation and rotation factors (Tunell, 1939). 1505 independent structure amplitudes (Table 2.4) were

obtained, which represents 51 % of the data accessible to Cu K_α radiation. No absorption corrections were applied to the data.

The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

2.3 Solution and Refinement of the Structure

In the space group Pbca, the equivalent positions are:-

$\pm$ (x, y, z), $\pm$ ($\frac{1}{2}$+x, $\frac{1}{2}$-y, -z), $\pm$ (-x, $\frac{1}{2}$+y, $\frac{1}{2}$-z), $\pm$ ($\frac{1}{2}$-x, -y, $\frac{1}{2}$+z).

A heavy atom situated in a general position will therefore give rise to the following sets of vectors:-

$\pm$ (2x, 2y, 2z)	single weight,
$\pm$ (2x, -2y, -2z)	single weight,
$\pm$ (-2x, 2y, -2z)	single weight,
$\pm$ (-2x, -2y, 2z)	single weight,
$\pm$ ($\frac{1}{2}$, $\frac{1}{2}$+2y, 2z)	double weight,
$\pm$ ($\frac{1}{2}$, $\frac{1}{2}$+2y, -2z)	double weight,
$\pm$ (2x, $\frac{1}{2}$, $\frac{1}{2}$+2z)	double weight,
$\pm$ (-2x, $\frac{1}{2}$, $\frac{1}{2}$+2z)	double weight,
$\pm$ ($\frac{1}{2}$+2x, 2y, $\frac{1}{2}$)	double weight,
$\pm$ ($\frac{1}{2}$+2x, -2y, $\frac{1}{2}$)	double weight,
$\pm$ ($\frac{1}{2}$, 0, $\frac{1}{2}$+2z)	quadruple weight,
$\pm$ ($\frac{1}{2}$+2x, $\frac{1}{2}$, 0)	quadruple weight,
$\pm$ (0, $\frac{1}{2}$+2y, $\frac{1}{2}$)	quadruple weight.

Thus in the three-dimensional Patterson summation, there are nine dominant peaks. Six peaks are on the Harker sections at u = $\frac{1}{2}$, v = $\frac{1}{2}$ and w = $\frac{1}{2}$ respectively and three are on the Harker lines at u = $\frac{1}{2}$, v = 0; v = $\frac{1}{2}$, w = 0 and w = $\frac{1}{2}$, u = 0 respectively.

The positions of the independent Harker peaks can thus be summarised as:-

Section	Two-fold Peaks	Four-fold Peaks
$u = \frac{1}{2}$	$\pm (\frac{1}{2}, \frac{1}{2}+2y, 2z)$	$\pm (\frac{1}{2}, 0, \frac{1}{2}+2z)$
	$\pm (\frac{1}{2}, \frac{1}{2}+2y, -2z)$	
$v = \frac{1}{2}$	$\pm (2x, \frac{1}{2}, \frac{1}{2}+2z)$	$\pm (\frac{1}{2}+2x, \frac{1}{2}, 0)$
	$\pm (-2x, \frac{1}{2}, \frac{1}{2}+2z)$	
$w = \frac{1}{2}$	$\pm (\frac{1}{2}+2x, 2y, \frac{1}{2})$	$\pm (0, \frac{1}{2}+2y, \frac{1}{2})$
	$\pm (\frac{1}{2}+2x, -2y, \frac{1}{2})$	

The peaks from any two Harker sections or all three Harker lines will suffice to determine the x, y and z coordinates of the heavy atom.

The asymmetric units of the three Harker sections of the three-dimensional Patterson function were calculated and interpreted on the basis of the analytical functions given. The values obtained for the coordinates of the bromide ion were:-

ATOM	X/a	Y/b	Z/c
Br(1)	0.0950	0.1684	0.2247

A set of structure factors, based on the coordinates of the bromide ion, was calculated and the calculated phase angles used in conjunction with the observed structure amplitudes to evaluate an electron density synthesis. The coordinates of the remaining atoms in the structure were obtained from this initial electron density synthesis. The different chemical species present in the structure

were differentiated on the basis of their peak height and a knowledge of the chemical structure. Inclusion of the remaining thirteen atoms (11 carbon and 2 nitrogen) in the structure factor calculation reduced the R-factor from 0.41, based on the bromide ion alone, to 0.274. Two further cycles of Fourier refinement reduced the R-factor to 0.227.

The structure was then refined in seven cycles of least-squares minimisation of the function $M = \sum w(|F_o| - |F_c|)^2$. D.R. Pollard's least-squares program, (1968) was used in the initial stages of the refinement. Each reciprocal lattice net was given an individual scale factor and each atom a single isotropic temperature factor. The observations were all given unit weight. After three cycles of full matrix refinement the R-factor was reduced to 0.178. A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 2/|F_o|_{max}$, which has been recommended by Cruickshank, (1961) for use with photographic data, was then applied and a further cycle of least-squares refinement calculated. The R-factor was reduced to 0.174.

The Glasgow S.F.L.S. program (Cruickshank and Smith, 1965) was then used to continue the refinement. On the assumption that the data were on the same relative scale at the conclusion of the isotropic refinement, individual anisotropic thermal parameters

and a single overall scale factor were refined. A further three cycles of refinement in which the block diagonal approximation to the normal matrix was applied produced convergence. The R-factor was reduced to 0.143. The weighting scheme applied in the last three cycles of refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$$

where $p_1 = 4$, $p_2 = 0.3$ and $p_3 = 0.001$.

In the final cycle of refinement, the shifts in positional and thermal parameters were not significant being less than one quarter of the corresponding standard deviations. The atomic scattering factors used throughout this analysis were those of Hoerni and Ibers, (1954) for carbon and nitrogen and those of Freeman and Watson, (1961) for bromine. The course of the analysis is summarised in Table 2.1.

Tables 2.2 and 2.3 contain the final values of the fractional atomic coordinates and anisotropic thermal parameters. The observed and final calculated structure amplitudes are given in Table 2.4. Atomic coordinates in Angstroms referred to orthogonal axes defined by X parallel to $\underline{a}^*$, Y normal to $\underline{a}^*$ and $\underline{c}$ and Z parallel to $\underline{c}$ are given in Table 2.5. Tables 2.6 and 2.7 contain the bond lengths and interbond angles in the structure. Table 2.8 lists intermolecular contacts between atoms which are less than 4 Å. In Table 2.9 the equations of the mean planes through portions

of the molecule are given together with the deviations of certain atoms from these planes. Estimated standard deviations, where quoted, are in units of the last decimal place of the quantity to which they refer.

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 2.1. The packing of the molecules in the unit cell, as viewed down the b-axis, is shown in Fig. 2.2.

TABLES AND DIAGRAMS

FIGURE 2.1

A molecular drawing illustrating the numbering of the non-hydrogen atoms in the structure.

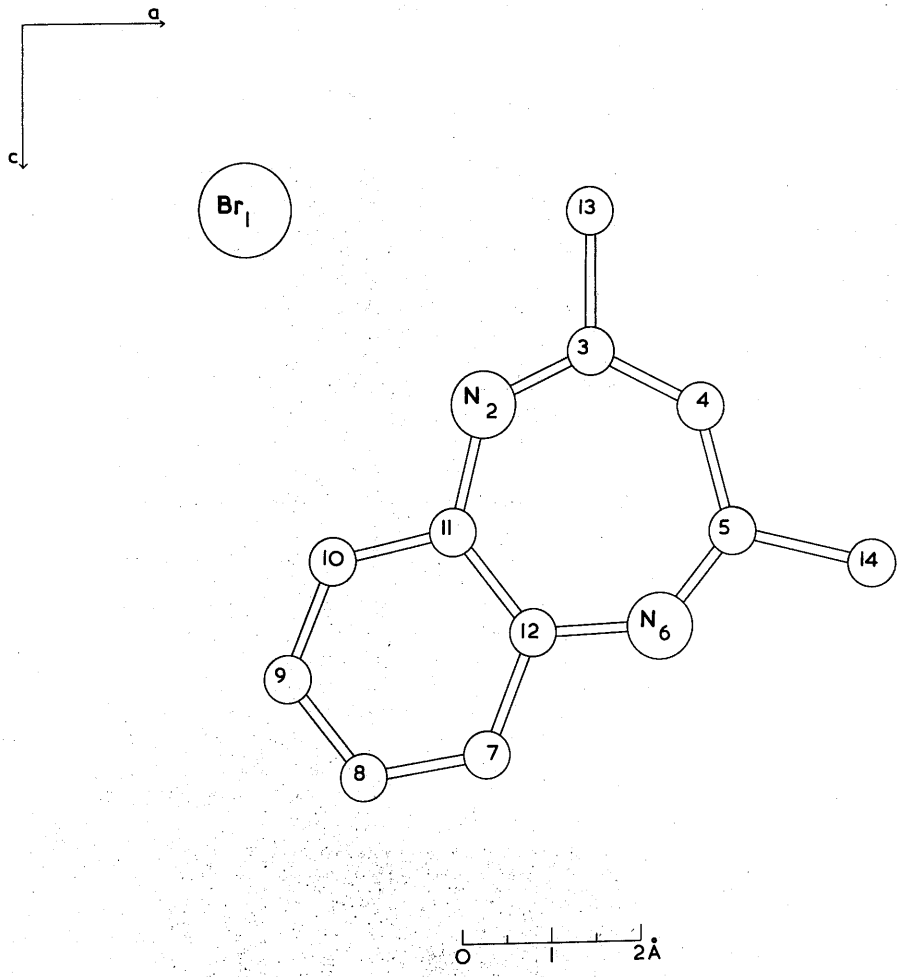

a
c
Br1
13
3
N2
4
11
5
14
10
12
N6
9
7
8
0
1
2Å

FIGURE 2.2

The molecular packing viewed down the b-axis.

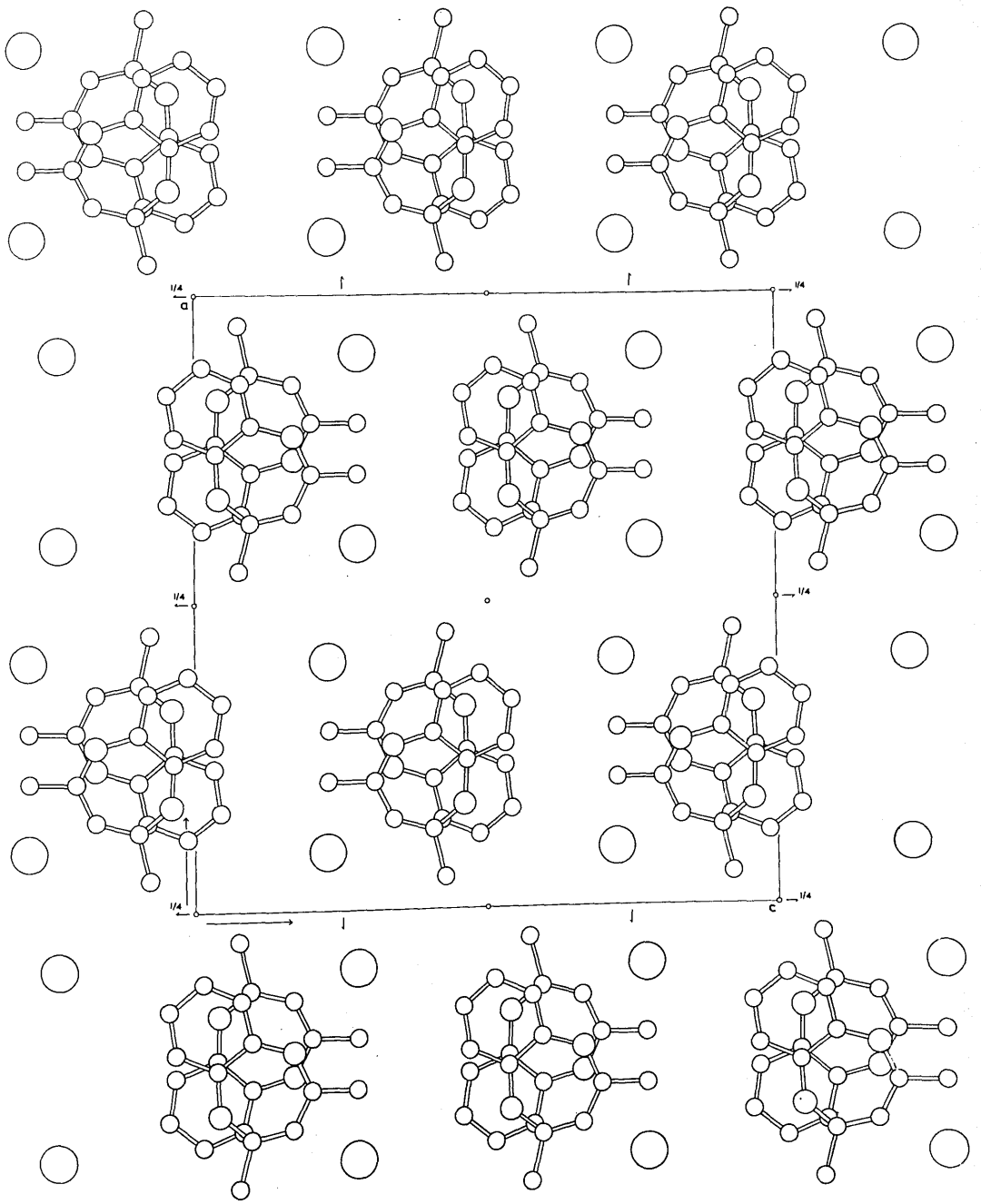

1/4
a
1/4
1/4
1/4
1/4
c
1/4

TABLE 2.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	Br	0.41
2	Br + 11 C + 2 N	0.274
3	Br + 11 C + 2 N	0.238
4	Br + 11 C + 2 N	0.227

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layers scales, unit weights	0.186
2	"	0.180
3	"	0.178
4	As above, weighting scheme 1 applied	0.174
5	Block diagonal, individual anisotropic temperature factors, overall scale factor, weighting scheme 2 applied	0.155
6	"	0.144
7	"	0.143

TABLE 2.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
Br(1)	0.0950 ± 1	0.1701 ± 3	0.2245 ± 1
N(2)	0.2310 ± 6	0.1504 ± 18	0.3347 ± 5
C(3)	0.2915 ± 7	0.1515 ± 21	0.3047 ± 6
C(4)	0.3537 ± 8	0.1511 ± 25	0.3367 ± 8
C(5)	0.3706 ± 7	0.1505 ± 21	0.4069 ± 8
N(6)	0.3302 ± 6	0.1435 ± 19	0.4604 ± 6
C(7)	0.2315 ± 7	0.1414 ± 23	0.5324 ± 7
C(8)	0.1611 ± 8	0.1426 ± 28	0.5433 ± 8
C(9)	0.1180 ± 8	0.1397 ± 29	0.4874 ± 9
C(10)	0.1442 ± 8	0.1456 ± 27	0.4218 ± 8
C(11)	0.2119 ± 7	0.1510 ± 21	0.4063 ± 7
C(12)	0.2578 ± 7	0.1498 ± 23	0.4642 ± 6
C(13)	0.2912 ± 9	0.1570 ± 27	0.2257 ± 8
C(14)	0.4488 ± 9	0.1411 ± 35	0.4264 ± 11

TABLE 2.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
Br(1)	0.0712 8	0.0616 10	0.0587 7	0.0007 15	-0.0037 14	-0.0026 16
N(2)	0.0590 65	0.0389 66	0.0446 49	-0.0063 100	0.0064 89	0.0212 110
C(3)	0.0651 70	0.0324 75	0.0389 54	0.0079 111	0.0257 101	0.0096 136
C(4)	0.0545 70	0.0482 94	0.0591 75	0.0006 140	0.0163 123	0.0094 141
C(5)	0.0587 74	0.0258 76	0.0627 69	0.0146 133	-0.0013 113	-0.0017 132
N(6)	0.0569 59	0.0388 76	0.0492 53	0.0032 104	-0.0052 89	0.0096 114
C(7)	0.0640 75	0.0352 87	0.0450 57	-0.0087 115	0.0230 101	-0.0111 126
C(8)	0.0710 82	0.0671 117	0.0548 73	0.0035 154	0.0514 129	0.0118 174
C(9)	0.0426 59	0.0826 122	0.0682 79	-0.0250 172	0.0308 120	0.0070 148
C(10)	0.0546 70	0.0555 101	0.0613 74	0.0014 140	0.0206 126	0.0194 149
C(11)	0.0520 62	0.0327 76	0.0555 62	-0.0014 124	0.0227 105	0.0016 129
C(12)	0.0523 60	0.0323 77	0.0473 56	0.0071 115	0.0018 99	0.0174 129
C(13)	0.0742 83	0.0693 107	0.0473 65	0.0091 154	0.0173 129	-0.0276 168
C(14)	0.0554 83	0.0914 149	0.0883 116	-0.0014 213	0.0031 157	-0.0147 191

TABLE 2.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES

H	K	L	F OBS	F CALC
8	0	0	69.3	60.7
10	0	0	90.4	76.6
12	0	0	38.0	41.4
14	0	0	24.7	17.8
16	0	0	107.2	73.7
20	0	0	24.4	28.5
22	0	0	15.2	17.1
0	0	2	68.9	87.5
2	0	2	113.2	112.9
4	0	2	95.0	100.5
5	0	2	21.6	21.4
6	0	2	186.8	187.0
7	0	2	42.0	41.3
8	0	2	35.9	29.3
9	0	2	79.2	84.2
10	0	2	203.5	182.2
11	0	2	23.4	12.3
12	0	2	40.3	41.1
13	0	2	73.1	65.7
14	0	2	15.0	10.8
15	0	2	7.7	3.0
16	0	2	84.9	72.6
17	0	2	14.1	11.4
18	0	2	30.8	22.9
19	0	2	9.5	7.0
20	0	2	33.3	31.3
22	0	2	19.1	19.3
1	0	4	99.4	103.4
2	0	4	34.0	21.6
3	0	4	215.3	205.4
4	0	4	101.6	105.4
6	0	4	149.7	145.1
8	0	4	11.5	4.3
9	0	4	56.7	59.8
10	0	4	124.1	113.0
11	0	4	27.8	26.0
12	0	4	88.1	69.0
13	0	4	53.6	46.6
14	0	4	50.8	53.7
15	0	4	44.4	44.8
17	0	4	12.3	15.5
19	0	4	16.3	21.7
20	0	4	18.9	16.0
22	0	4	6.2	6.3
0	0	6	4.6	7.0
0	0	6	118.0	124.2
1	0	6	87.4	92.3
2	0	6	82.5	86.8
3	0	6	134.1	147.5
5	0	6	12.8	16.9
7	0	6	128.0	116.8
8	0	6	30.0	33.0
9	0	6	101.0	82.9
10	0	6	74.6	66.1
11	0	6	27.5	34.0
12	0	6	15.4	13.3
13	0	6	53.1	52.1
14	0	6	7.8	6.8
15	0	6	38.9	41.0
16	0	6	30.0	30.6
17	0	6	28.9	28.2
19	0	6	27.7	26.7
20	0	6	22.5	19.1
21	0	6	4.9	3.7
22	0	6	10.6	11.9
23	0	6	13.3	15.3
0	0	8	35.8	33.0
1	0	8	119.4	113.4
2	0	8	61.1	56.6
3	0	8	128.5	125.9
4	0	8	52.3	47.3
5	0	8	21.0	31.4
6	0	8	45.3	54.1
8	0	8	25.1	17.0
9	0	8	92.1	85.5
10	0	8	66.1	57.4
12	0	8	6.0	1.4
13	0	8	113.2	99.2
14	0	8	8.9	15.4
15	0	8	7.6	12.8
16	0	8	33.2	26.0
17	0	8	34.2	26.1
19	0	8	10.2	11.0
0	0	10	12.4	12.1
1	0	10	143.8	149.4
2	0	10	15.2	21.5
3	0	10	107.6	117.1
5	0	10	18.9	31.0
6	0	10	25.8	13.4
7	0	10	104.7	91.7
8	0	10	6.5	3.7
9	0	10	60.6	60.4
10	0	10	52.9	41.8
11	0	10	17.0	22.3
12	0	10	48.1	46.5
13	0	10	29.1	28.3
14	0	10	12.3	15.6
15	0	10	56.4	46.5
17	0	10	27.9	32.2
19	0	10	28.7	31.3
1	0	12	92.2	96.6
2	0	12	14.1	6.3
3	0	12	84.1	88.1
4	0	12	9.2	9.7
5	0	12	18.0	23.1
7	0	12	76.1	77.8
8	0	12	19.1	15.9
9	0	12	85.4	76.0
10	0	12	27.8	28.8
11	0	12	49.1	42.6
12	0	12	49.7	40.7
13	0	12	52.2	42.5
14	0	12	21.2	27.4
15	0	12	20.4	15.7
16	0	12	8.3	15.0
17	0	12	11.2	17.0
19	0	12	12.4	34.0
0	0	14	25.0	27.0
1	0	14	27.5	19.1
2	0	14	58.5	56.7
3	0	14	56.8	52.8
4	0	14	51.6	54.1
5	0	14	27.2	26.3
6	0	14	54.5	42.8
7	0	14	48.4	34.0
9	0	14	73.2	65.6
H	K	L	F OBS	F CALC
10	0	14	45.2	43.4
11	0	14	28.9	17.9
13	0	14	46.8	36.4
14	0	14	16.7	14.4
16	0	14	13.9	14.8
17	0	14	14.7	13.5
19	0	14	15.5	16.2
20	0	14	5.0	9.7
0	0	16	115.7	104.4
1	0	16	29.6	29.1
2	0	16	5.7	11.5
3	0	16	51.5	47.9
4	0	16	34.5	32.5
6	0	16	58.3	52.0
7	0	16	17.4	22.9
8	0	16	20.1	19.5
9	0	16	28.1	24.7
10	0	16	31.6	25.3
11	0	16	18.9	14.9
12	0	16	19.6	22.1
14	0	16	8.3	7.9
15	0	16	5.8	7.6
16	0	16	25.2	22.6
17	0	16	6.4	8.2
0	0	18	41.2	44.3
1	0	18	14.2	18.1
2	0	18	22.2	22.2
4	0	18	35.1	38.0
6	0	18	36.2	36.4
7	0	18	7.9	9.2
8	0	18	7.7	11.5
9	0	18	31.5	32.4
12	0	18	21.7	20.0
14	0	18	12.0	12.1
15	0	18	1.9	4.7
16	0	18	16.4	17.1
0	0	20	38.9	42.0
2	0	20	7.1	14.0
3	0	20	4.6	0.4
4	0	20	22.4	22.0
7	0	20	37.5	36.6
8	0	20	5.0	2.8
10	0	20	15.5	19.6
12	0	20	14.5	13.7
14	0	20	3.6	7.0
0	0	22	44.1	32.1
3	0	22	7.0	9.1
4	0	22	23.4	20.2
6	0	22	14.4	14.6
7	0	22	7.5	9.3
9	0	22	9.6	10.6
10	0	22	16.5	18.2
0	0	24	3.7	5.7
1	0	24	8.6	10.6
2	0	24	10.0	10.9
3	0	24	10.2	8.9
4	0	24	5.0	9.0
4	1	0	124.6	134.7
5	1	0	108.4	97.7
8	1	0	189.5	178.5
10	1	0	19.4	9.8
12	1	0	66.6	63.7
14	1	0	90.3	85.2
16	1	0	11.1	15.2
18	1	0	30.9	33.4
20	1	0	17.6	15.4
22	1	0	7.9	10.2
0	1	1	0.4	4.2
1	1	1	60.2	62.7
4	1	1	86.5	97.9
9	1	1	23.2	32.3
10	1	1	25.5	15.9
11	1	1	28.8	20.9
12	1	1	37.6	39.6
13	1	1	6.2	8.5
14	1	1	46.6	42.7
16	1	1	13.9	9.2
18	1	1	15.8	16.0
20	1	1	8.7	11.1
22	1	1	6.0	6.2
1	1	2	4.4	6.6
2	1	2	131.1	127.6
3	1	2	33.5	38.3
4	1	2	191.5	190.6
5	1	2	72.6	75.6
6	1	2	72.1	67.3
7	1	2	16.2	11.9
8	1	2	112.3	107.2
9	1	2	19.4	14.1
10	1	2	75.7	64.9
11	1	2	25.8	20.9
12	1	2	85.4	72.0
13	1	2	71.1	66.3
14	1	2	28.0	24.5
15	1	2	29.1	23.2
16	1	2	27.1	24.7
17	1	2	6.5	9.4
18	1	2	10.3	12.1
19	1	2	14.7	17.7
20	1	2	107.3	114.1
1	1	3	93.5	90.0
3	1	3	43.3	47.2
4	1	3	29.4	26.5
5	1	3	31.3	31.5
6	1	3	29.5	15.4
7	1	3	31.3	28.6
8	1	3	34.8	36.1
9	1	3	19.1	23.7
10	1	3	9.9	14.9
11	1	3	6.0	7.1
12	1	3	7.3	12.0
13	1	3	4.2	3.6
14	1	3	64.3	72.9
15	1	3	32.8	22.4
16	1	3	33.1	21.1
17	1	3	80.2	77.5
18	1	3	65.9	58.4
19	1	3	15.4	15.5
20	1	3	16.4	20.0
1	1	4	65.2	64.9
2	1	4	57.9	54.6
3	1	4	49.6	37.0
4	1	4	5.9	5.2
5	1	4	47.4	48.2
6	1	4	23.3	22.9
7	1	4	15.4	15.5
8	1	4	13.1	13.7
21	1	4	13.1	11.2
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6	1	5	37.6	30.8
7	1	5	27.5	31.1
8	1	5	66.1	74.9
9	1	5	16.9	30.9
10	1	5	35.7	38.8
11	1	5	11.5	17.4
13	1	5	43.6	46.5
14	1	5	50.6	35.3
15	1	5	11.4	11.1
16	1	5	11.8	7.2
17	1	5	12.2	17.9
19	1	5	21.7	17.7
20	1	5	26.1	26.6
21	1	5	21.7	21.6
22	1	5	5.9	8.9
1	1	6	147.6	139.9
2	1	6	79.1	86.0
3	1	6	71.6	72.5
4	1	6	17.7	26.4
5	1	6	74.6	68.8
6	1	6	37.4	42.9
8	1	6	82.2	73.8
9	1	6	33.4	44.0
10	1	6	45.8	40.2
11	1	6	34.1	40.6
12	1	6	84.3	68.0
13	1	6	44.4	41.0
14	1	6	24.0	24.0
15	1	6	51.0	41.0
16	1	6	68.7	59.2
17	1	6	17.1	17.8
18	1	6	15.8	17.1
19	1	6	34.6	35.0
20	1	6	7.0	9.5
21	1	6	22.4	22.0
22	1	6	8.6	8.0
0	1	7	37.6	36.6
1	1	7	88.1	78.6
2	1	7	74.2	67.3
3	1	7	2.3	0.4
4	1	7	96.8	80.2
5	1	7	38.1	43.3
6	1	7	11.8	12.9
7	1	7	48.9	40.5
8	1	7	7.5	18.6
9	1	7	37.0	33.6
10	1	7	11.4	2.5
11	1	7	11.8	8.0
12	1	7	12.3	12.9
13	1	7	3.1	7.8
1	1	8	94.8	102.0
2	1	8	56.7	55.8
3	1	8	41.0	30.8
4	1	8	43.8	36.1
5	1	8	82.0	170.4
6	1	8	5.6	6.8
7	1	8	40.2	36.6
8	1	8	40.3	32.5
9	1	8	67.2	71.5
10	1	8	6.6	6.2
11	1	8	73.1	74.6
12	1	8	19.5	20.5
13	1	8	17.0	18.9
14	1	8	36.4	34.1
15	1	8	15.7	14.2
16	1	8	8.8	9.0
18	1	8	15.6	16.5
19	1	8	48.4	46.7
20	1	8	12.6	2.3
21	1	8	8.1	3.0
22	1	8	36.8	39.0
1	1	9	72.9	66.9
2	1	9	15.4	7.2
3	1	9	24.4	28.0
4	1	9	10.8	14.1
5	1	9	45.6	34.2
6	1	9	4.2	1.4
7	1	9	43.5	36.0
8	1	9	6.9	15.8
9	1	9	18.4	15.3
10	1	9	37.9	29.4
11	1	9	9.3	9.9
12	1	9	9.2	11.4
13	1	9	98.5	91.2
14	1	9	39.9	40.2
15	1	9	96.0	88.3
16	1	9	52.4	50.0
17	1	9	15.7	6.8
18	1	9	56.0	53.9
19	1	9	66.1	57.7
20	1	9	24.6	31.5
21	1	9	63.2	55.5
22	1	9	21.0	17.8
1	1	10	37.9	19.8
2	1	10	21.9	19.8
3	1	10	39.9	40.2
4	1	10	96.0	88.3
5	1	10	52.4	50.0
6	1	10	15.7	6.8
7	1	10	56.0	53.9
8	1	10	66.1	57.7
9	1	10	24.6	31.5
10	1	10	63.2	55.5
11	1	10	21.0	17.8
12	1	10	21.9	19.8
13	1	10	37.9	19.8
14	1	10	39.9	40.2
15	1	10	96.0	88.3
16	1	10	52.4	50.0
17	1	10	15.7	6.8
18	1	10	56.0	53.9
19	1	10	66.1	57.7
20	1	10	24.6	31.5
21	1	10	63.2	55.5
22	1	10	21.0	17.8
1	1	11	32.5	33.6
2	1	11	23.0	18.1
3	1	11	19.3	22.1
4	1	11	7.7	7.4
5	1	11	4.8	5.6
6	1	11	4.6	4.1
7	1	11	110.3	99.3
8	1	11	40.2	31.9
9	1	11	33.2	29.8
10	1	11	5.9	5.2
11	1	11	47.4	48.2
12	1	11	18.9	22.9
13	1	11	15.4	15.5
14	1	11	13.1	13.7
15	1	11	64.7	57.7
12	1	12	21.1	15.2
14	1	12	6.1	6.3
15	1	12	32.2	29.7
17	1	12	10.0	14.6
18	1	12	12.6	10.7
19	1	12	12.1	8.3
21	1	12	10.1	10.4
1	1	13	27.0	32.2
2	1	13	12.6	17.1
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6	1	13	11.7	22.9
7	1	13	12.7	9.4
9	1	13	6.0	7.4
11	1	13	29.7	22.6
13	1	13	13.6	14.8
14	1	13	5.3	8.4
19	1	13	5.1	3.8
1	1	14	43.6	44.1
2	1	14	64.7	51.1
3	1	14	5.7	7.2
4	1	14	25.7	26.7
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6	1	14	47.7	38.6
8	1	14	27.0	23.1
9	1	14	4.7	11.7
10	1	14	12.6	14.9
11	1	14	37.8	35.2
12	1	14	24.6	25.0
14	1	14	16.3	16.4
15	1	14	14.4	16.1
17	1	14	10.1	13.0
18	1	14	4.4	7.1
1	1	15	28.5	22.7
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3	1	15	8.4	6.8
4	1	15	5.4	8.5
5	1	15	46.5	39.0
6	1	15	15.6	13.5
7	1	15	7.2	13.6
8	1	15	30.9	18.4
9	1	15	8.7	8.4
11	1	15	25.8	20.5
12	1	15	8.5	12.2
13	1	15	10.0	12.8
15	1	15	5.6	6.1
1	1	16	34.5	34.7
2	1	16	36.1	40.5
3	1	16	20.0	19.4
4	1	16	26.0	31.2
5	1	16	40.4	39.2
6	1	16	51.5	51.2
10	1	16	5.4	4.3
11	1	16	31.8	22.1
12	1	16	11.5	17.7
13	1	16	5.5	7.0
14	1	16	24.5	20.9
15	1	16	13.8	15.5
17	1	16	9.1	5.2
18	1	16	15.5	15.7
2	1	17	11.7	10.6
4	1	17	21.9	24.0
6	1	17	35.8	31.1
12	1	17	12.7	12.6
17	1	17	4.5	5.4
2	1	18	45.0	39.0
3	1	18	15.7	15.0
4	1	18	31.6	28.4
5	1	18	10.8	9.4
6	1	18	12.3	10.8
7	1	18	18.5	16.7
8	1	18	42.8	36.5
9	1	18	4.4	5.7
10	1	18	10.5	9.8
11	1	18	10.1	9.4
12	1	18	22.4	21.6
13	1	18	19.3	14.9
16	1	18	4.8	6.8
2	1	19	26.0	28.2
4	1	19	7.9	7.6
6	1	19	8.1	10.3
7	1	19	7.1	5.9
8	1	19	14.7	18.0
9	1	19	11.4	12.7
10	1	19	33.6	32.7
11	1	19	25.8	20.4
12	1	19	6.5	4.3
13	1	19	7.6	10.3
14	1	19	27.5	26.4
15	1	19	10.7	10.6
16	1	19	11.9	14.2
2	1	20	9.1	8.9
4	1	20	12.8	12.9
6	1	20	4.3	7.4
8	1	20	9.1	10.2
12	1	20	4.4	6.9
1	1	22	9.0	9.0
2	1	22	20.7	19.1
4	1	22	17.1	15.9
5	1	22	8.9	9.7
6	1	22	9.6	8.7
10	1	22	12.2	17.5
12	1	22	4.5	6.6
1	1	23	9.2	9.9
2	1	23	3.7	2.2
5	1	23	6.6	8.2
1	1	24	3.0	6.8
2	1	24	8.3	10.6
2	2	0	37.3	23.2
4	2	0	66.1	84.1
8	2	0	12.9	15.6
10	2	0	53.1	50.1
12	2	0	19.4	26.3
14	2	0	9.5	9.7
16	2	0	13.4	13.8
20	2	0	19.1	13.0
22	2	0	6.1	8.6
1	2	1	230.2	236.3
2	2	1	23.2	32.3
3	2	1	38.4	47.1
5	2	1	40.0	24.1
6	2	1	142.2	137.4
7	2	1	18.9	7.8
9	2	1	30.1	16.0
11	2	1	45.1	43.9
12	2	1	92.2	92.1
11	2	2	31.6	26.8
13	2	2	14.5	21.4
15	2	2	22.7	22.0
16	2	2	62.9	54.2
17	2	2	6.0	3.6
18	2	2	10.8	8.6
19	2	2	5.3	11.0
20	2	2	23.7	24.2
21	2	2	13.5	14.3
22	2	2	68.7	69.1
2	2	3	40.3	38.5
3	2	3	38.8	37.5
4	2	3	60.9	57.8
5	2	3	8.4	7.9
6	2	3	86.6	81.5
7	2	3	19.3	17.7
8	2	3	5.2	3.1
9	2	3	37.0	29.5
10	2	3	86.3	70.7
12	2	3	26.5	24.2
13	2	3	18.0	22.6
14	2	3	5.6	11.8
16	2	3	36.4	31.0
3	2	4	4.3	6.2
4	2	4	4.2	8.1
20	2	4	10.0	13.5
22	2	4	6.2	8.7
1	2	5	74.9	67.3
3	2	5	70.0	73.3
5	2	5	34.4	41.0
7	2	5	100.0	87.5
9	2	5	9.1	0.7
11	2	5	43.0	52.2
13	2	5	26.3	30.6
15	2	5	134.1	114.9
17	2	5	61.4	54.0
19	2	5	73.2	57.1
21	2	5	41.6	26.0
23	2	5	58.2	51.3
3	2	6	11.3	15.0
5	2	6	16.5	15.7
7	2	6	8.9	8.6
9	2	6	76.7	69.2
11	2	6	31.5	40.1
13	2	6	28.0	21.6
15	2	6	57.5	69.4
17	2	6	40.3	46.9
19	2	6	59.0	63.6
21	2	6	82.5	39.1
1	2	7	41.5	29.3
3	2	7	49.6	49.2
5	2	7	28.4	24.1
7	2	7	18.4	22.4
9	2	7	22.0	18.0
11	2	7	27.0	23.2
13	2	7	16.5	15.7
15	2	7	31.5	41.3
17	2	7	33.9	27.8
19	2	7	74.7	67.3
21	2	7	27.0	23.2
1	2	8	94.8	102.0
3	2	8	56.7	55.8
5	2	8	41.0	30.8
7	2	8	43.8	36.1
9	2	8	82.0	170.4
11	2	8	5.6	6.8
13	2	8	40.2	36.6
15	2	8	40.3	32.5
17	2	8	67.2	71.5
19	2	8	6.6	6.2
21	2	8	73.1	74.6
23	2	8	19.5	20.5
1	2	9	17.0	18.9
3	2	9	36.4	34.1
5	2	9	15.7	14.2
7	2	9	8.8	9.0
9	2	9	15.6	16.5
11	2	9	48.4	46.7
13	2	9	12.6	2.3
15	2	9	8.1	3.0
17	2	9	40.3	32.5
19	2	9	67.2	71.5
21	2	9	6.6	6.2
1	2	10	6.9	0.0
3	2	10	17.8	11.0
5	2	10	19.0	12.6
7	2	10	9.4	10.5
9	2	10	9.6	11.0
11	2	10	33.6	33.2
13	2	10	9.4	10.5
15	2	10	22.1	25.3
17	2	10	31.3	28.7
19	2	10	26.2	23.1
21	2	10	6.9	0.0
2	2	11	52.3	56.9
4	2	11	19.0	12.6
6	2	11	14.9	3.0
8	2	11	57.6	56.8
10	2	11	17.9	11.8
12	2	11	40.3	34.9
14	2	11	33.6	33.2
16	2	11	9.

H	K	L	F OBS	F CALC
3	2	17	10.4	9.4
4	2	17	19.5	20.2
5	2	17	6.0	6.9
6	2	17	43.7	34.9
7	2	17	25.0	17.7
8	2	17	5.6	8.8
9	2	17	10.3	4.7
10	2	17	19.6	24.7
12	2	17	19.6	17.0
14	2	17	5.9	7.8
15	2	17	4.5	8.8
16	2	17	14.4	14.0
9	2	18	21.9	22.3
1	2	19	9.1	9.3
2	2	19	7.3	9.6
4	2	19	17.8	18.7
6	2	19	35.9	25.6
8	2	19	40.0	28.4
10	2	19	22.4	19.2
12	2	19	18.3	12.7
14	2	19	9.7	6.7
0	2	20	24.3	20.4
2	2	20	9.3	9.8
4	2	20	9.4	11.3
6	2	20	16.8	16.3
10	2	20	10.8	10.6
12	2	20	4.5	8.7
0	2	21	27.6	26.6
1	2	21	6.0	9.1
3	2	21	8.0	4.3
4	2	21	17.4	15.6
5	2	21	4.0	4.9
6	2	21	14.4	16.1
9	2	21	5.8	8.4
10	2	21	12.5	14.0
11	2	21	6.1	6.1
0	2	22	19.9	13.6
2	2	22	7.1	8.5
6	2	22	7.7	9.4
0	2	23	11.1	13.8
3	2	23	3.5	7.9
1	2	24	8.2	15.2
5	2	23	21.0	5.2
6	2	23	10.5	12.6
2	3	0	14.8	13.5
4	3	0	13.1	12.6
6	3	0	18.5	4.2
8	3	0	15.3	8.1
12	3	0	19.8	10.0
1	3	1	35.8	30.2
2	3	1	113.2	108.4
3	3	1	11.4	12.5
4	3	1	45.1	35.0
6	3	1	57.4	63.8
9	3	1	19.1	24.8
10	3	1	22.8	22.6
11	3	1	38.9	24.9
12	3	1	46.5	42.0
13	3	1	10.5	9.2
15	3	1	7.2	5.6
15	3	1	7.8	4.2
16	3	1	18.8	14.6
15	3	1	29.8	27.2
20	3	1	16.5	17.6
21	3	1	9.6	8.5
22	3	1	7.6	10.3
1	3	2	72.1	71.7
2	3	2	23.0	23.7
3	3	2	8.8	8.8
5	3	2	9.4	1.1
9	3	2	24.5	13.5
10	3	2	12.6	8.9
11	3	2	17.3	12.3
2	3	3	140.4	144.3
3	3	3	29.8	28.8
4	3	3	126.3	114.7
5	3	3	88.9	88.8
7	3	3	9.2	12.3
8	3	3	59.3	57.1
9	3	3	43.4	33.2
10	3	3	51.6	48.7
11	3	3	17.2	31.3
12	3	3	48.4	47.1
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14	3	3	55.0	54.8
16	3	3	28.0	29.8
17	3	3	24.4	24.2
18	3	3	8.8	12.4
19	3	3	8.2	10.4
20	3	3	21.5	19.4
21	3	3	9.7	9.1
22	3	3	8.7	9.3
1	3	4	19.2	14.4
2	3	4	11.6	5.2
3	3	4	12.8	5.8
4	3	4	12.2	5.7
5	3	4	4.2	4.2
6	3	4	9.5	14.8
8	3	4	18.5	9.8
9	3	4	10.5	5.8
10	3	4	18.5	9.5
12	3	4	67.5	67.8
1	3	5	44.2	48.1
2	3	5	59.1	59.8
3	3	5	26.6	32.6
4	3	5	21.8	21.5
5	3	5	40.1	47.3
6	3	5	60.8	51.3
7	3	5	33.8	32.4
8	3	5	19.4	18.4
9	3	5	34.0	29.8
10	3	5	23.1	21.4
11	3	5	42.5	37.6
12	3	5	78.2	72.9
13	3	5	19.8	18.4
14	3	5	15.9	15.2
15	3	5	14.5	15.8
16	3	5	23.1	21.4
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21	3	22	7.8	8.4
22	3	22	7.8	8.4

H	K	L	F OBS	F CALC
14	4	9	12.0	13.0
15	4	9	20.2	19.9
17	4	9	18.8	17.3
19	4	9	16.7	15.3
0	4	10	10.2	5.8
1	4	10	41.7	46.4
2	4	10	9.8	9.8
3	4	10	21.7	25.2
4	4	10	17.3	8.5
7	4	10	23.3	22.8
9	4	10	10.2	10.4
10	4	10	27.3	21.5
12	4	10	27.5	26.7
14	4	10	9.1	10.3
15	4	10	19.2	18.7
17	4	10	12.5	10.9
19	4	10	7.8	9.4
0	4	11	16.4	8.6
1	4	11	52.7	49.3
2	4	11	8.1	4.1
3	4	11	68.2	68.7
4	4	11	62.9	48.0
9	4	11	12.2	38.9
10	4	11	21.4	18.4
11	4	11	29.2	23.7
12	4	11	12.4	14.8
14	4	11	6.3	7.3
15	4	11	15.4	17.3
17	4	11	12.0	10.7
19	4	11	14.3	13.9
1	4	12	37.1	29.9
2	4	12	7.5	8.4
3	4	12	17.3	20.4
4	4	12	9.3	8.1
7	4	12	20.2	19.7
8	4	12	6.8	8.1
9	4	12	22.4	22.8
11	4	12	21.0	17.8
12	4	12	21.5	19.9
13	4	12	8.1	9.1
14	4	12	12.0	13.8
0	4	13	16.8	12.3
1	4	13	39.3	37.8
2	4	13	20.0	16.6
3	4	13	33.9	32.2
4	4	13	19.0	15.0
5	4	13	12.5	12.5
6	4	13	25.3	20.5
7	4	13	42.9	30.3
8	4	13	42.0	34.2
9	4	13	20.9	19.2
11	4	13	26.6	26.0
12	4	13	9.4	13.7
13	4	13	18.1	18.4
14	4	13	12.1	12.4
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2	4	14	28.7	24.9
3	4	14	13.5	9.7
4	4	14	19.6	18.9
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7	4	14	5.5	4.7
9	4	14	27.6	22.8
11	4	14	15.3	14.7
12	4	14	14.8	11.8
15	4	14	38.6	40.9
17	4	14	38.9	33.1
18	4	14	26.6	27.6
19	4	14	20.3	19.2
0	4	15	38.9	40.9
4	4	15	30.4	24.0
5	4	15	7.8	13.1
6	4	15	6.5	6.3
9	4	15	28.9	26.4
10	4	15	19.3	17.6
11	4	15	8.3	10.9
0	4	16	52.6	40.3
1	4	16	9.4	8.1
2	4	16	13.3	13.2
3	4	16	23.3	14.9
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6	4	16	19.2	15.2
8	4	16	16.3	10.3
9	4	16	6.0	8.8
10	4	16	7.0	6.7
0	4	17	40.1	36.1
1	4	17	24.6	18.9
3	4	17	7.3	8.8
4	4	17	17.8	17.3
6	4	17	37.9	26.3
7	4	17	12.3	11.9
9	4	17	8.5	8.3
10	4	17	17.3	13.9
12	4	17	11.5	11.4
1	4	18	9.9	8.6
2	4	18	4.9	8.3
3	4	18	11.7	12.0
6	4	18	8.0	8.7
7	4	19	27.3	23.1
9	4	19	31.9	30.5
10	4	19	28.4	19.5
12	4	19	27.7	20.6
13	4	19	14.5	12.3
15	4	19	7.7	8.3
17	4	19	7.5	8.0
1	4	20	8.0	13.7
3	4	20	9.8	11.4
4	4	20	45.2	34.3
5	4	20	17.4	17.9
7	4	20	5.8	8.7
9	4	20	120.0	108.7
10	4	20	8.0	17.3
11	4	20	21.2	19.9
12	4	20	13.8	13.9
13	4	20	16.

TABLE 2.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X	Y	Z
Br(1)	1.865 ± 2	1.183 ± 2	4.284 ± 2
N(2)	4.532 ± 12	1.046 ± 13	6.387 ± 11
C(3)	5.719 ± 14	1.054 ± 15	5.815 ± 12
C(4)	6.940 ± 15	1.051 ± 18	6.425 ± 15
C(5)	7.273 ± 14	1.047 ± 15	7.765 ± 15
N(6)	6.480 ± 12	0.998 ± 13	8.785 ± 11
C(7)	4.542 ± 14	0.984 ± 16	10.160 ± 13
C(8)	3.161 ± 17	0.992 ± 20	10.368 ± 16
C(9)	2.316 ± 15	0.973 ± 20	9.301 ± 17
C(10)	2.830 ± 15	1.013 ± 19	8.048 ± 15
C(11)	4.159 ± 14	1.051 ± 15	7.754 ± 14
C(12)	5.059 ± 13	1.042 ± 16	8.858 ± 12
C(13)	5.715 ± 17	1.092 ± 19	4.306 ± 15
C(14)	8.805 ± 18	0.981 ± 24	8.137 ± 21

TABLE 2.6

BOND LENGTHS AND E.S.D.S.

N(2) - C(3)	1.318 ± 18 Å	N(6) - C(12)	1.424 ± 18 Å
N(2) - C(11)	1.417 ± 17	C(7) - C(8)	1.397 ± 22
C(3) - C(4)	1.364 ± 21	C(7) - C(12)	1.402 ± 18
C(3) - C(13)	1.509 ± 19	C(8) - C(9)	1.362 ± 23
C(4) - C(5)	1.381 ± 21	C(9) - C(10)	1.355 ± 22
C(5) - N(6)	1.293 ± 18	C(10)- C(11)	1.362 ± 20
C(5) - C(14)	1.578 ± 23	C(11)- C(12)	1.424 ± 19

TABLE 2.7

INTERBOND ANGLES AND E.S.D.S.

C(3) - N(2) - C(11)	131.0 ± 12°	C(7) - C(8) - C(9)	119.8 ± 14°
N(2) - C(3) - C(4)	127.7 ± 12	C(8) - C(9) - C(10)	119.3 ± 14
N(2) - C(3) - C(13)	115.6 ± 12	C(9) - C(10)- C(11)	124.8 ± 14
C(4) - C(3) - C(13)	116.8 ± 13	N(2) - C(11)- C(10)	117.8 ± 13
C(3) - C(4) - C(5)	130.5 ± 14	N(2) - C(11)- C(12)	125.6 ± 12
C(4) - C(5) - N(6)	128.2 ± 14	C(10)- C(11)- C(12)	116.7 ± 13
C(4) - C(5) - C(14)	117.6 ± 14	N(6) - C(12)- C(7)	114.4 ± 11
N(6) - C(5) - C(14)	114.1 ± 13	N(6) - C(12)- C(11)	126.2 ± 11
C(5) - N(6) - C(12)	130.6 ± 12	C(7) - C(12)- C(11)	119.2 ± 12
C(8) - C(7) - C(12)	120.2 ± 13		

TABLE 2.8

INTERMOLECULAR CONTACTS BELOW 4 Å

C(10)....C(5)	ii	3.47 Å	C(13)....C(13)	ii	3.84 Å
C(12)....C(12)	ii	3.49	C(3).....C(3)	ii	3.84
C(5).....C(10)	ii	3.54	C(11)....C(5)	ii	3.84
N(2).....C(3)	ii	3.55	N(6).....C(12)	ii	3.85
C(7).....C(7)	ii	3.55	N(2).....C(4)	ii	3.85
N(2).....N(2)	ii	3.56	C(4).....N(2)	ii	3.86
C(3).....N(2)	ii	3.56	C(4).....C(10)	ii	3.87
N(6).....C(10)	ii	3.58	C(5).....C(9)	ii	3.88
C(10)....N(6)	ii	3.61	C(9).....C(14)	ii	3.89
C(9).....N(6)	ii	3.64	N(2).....C(11)	ii	3.90
C(7).....C(12)	ii	3.67	C(14)....C(10)	ii	3.90
N(6).....C(11)	ii	3.67	C(14)....C(9)	ii	3.90
N(6).....C(9)	ii	3.69	C(11)....N(2)	ii	3.91
C(12)....C(11)	ii	3.69	Br(1)....C(8)	iii	3.92
C(11)....C(12)	ii	3.71	C(7).....N(6)	ii	3.92
C(9).....C(5)	ii	3.74	C(12)....N(6)	ii	3.92
C(11)....N(6)	ii	3.77	C(11)....C(4)	ii	3.94
C(12)....C(7)	ii	3.78	C(4).....C(11)	ii	3.94
C(11)....C(11)	ii	3.79	N(6).....C(7)	ii	3.95
C(10)....C(4)	ii	3.80	C(10)....C(14)	ii	3.96

C(8).....N(6)	ii	3.82 Å	C(14)....C(14)	i	3.97 Å
N(6).....C(8)	ii	3.83	C(11)....C(3)	ii	3.98
C(5).....C(11)	ii	3.83	C(3).....C(11)	ii	3.99

Roman numerals refer to the transformations of the fractional coordinates given in Table 2.2.

i $1 - x, \quad -y, \; 1 - z;$ iii $x, \; \frac{1}{2} - y, -\frac{1}{2} + z;$

ii $\frac{1}{2} - x, -\frac{1}{2} + y, \quad z;$

The transformations are applied to the coordinates of the second atom in each case.

TABLE 2.9

MEAN MOLECULAR PLANES

(A) ATOMS DEFINING PLANES

PLANE NO.	ATOMS DEFINING PLANE
1	C(7), C(8), C(9) and C(10)
2	C(7), C(8), C(9), C(10), C(11) and C(12)
3	N(2), N(6), C(7), C(8), C(9), C(10), C(11) and C(12)
4	N(2), C(3), C(4), C(11) and C(13)
5	C(3), C(4), C(5), N(6) and C(14)
6	N(2), C(3), C(4), C(5), N(6), C(11), C(12), C(13) and C(14)
7	N(2), C(3), C(4), C(5), N(6), C(7), C(8), C(9), C(10), C(11), C(12), C(13) and C(14)

(B) PLANE EQUATIONS

PLANE NO.	P	Q	R	S	RMS D
1	0.0072	-0.9999	-0.0130	-1.0901	0.011
2	0.0171	-0.9996	-0.0214	-1.1396	0.012
3	0.0046	-0.9998	-0.0170	-1.1410	0.018
4	-0.0032	-0.9999	-0.0138	-1.1609	0.009
5	-0.0092	-0.9998	-0.0177	-1.2219	0.017
6	-0.0099	-0.9998	-0.0142	-1.2018	0.016
7	-0.0016	-0.9998	-0.0183	-1.1767	0.019

P, Q and R are the direction cosines of the plane normal, S is the plane to origin distance and RMS D is the root mean square deviation of the atoms defining the plane, from the plane, in Angstroms. The plane equation is then

$$PX + QY + RZ = S$$

where X, Y and Z are coordinates in Angstroms referred to standard orthogonal axes.

(C) DEVIATIONS FROM PLANES (Å)

PLANE NO. ATOM	1	2	3	4	5	6	7
Br(1)	-	-	-	-	-	-	-
N(2)	-0.007	0.035	0.007	0.012	0.021	0.020	0.007
C(3)	0.001	0.060	0.015	0.008	0.012	0.009	0.007
C(4)	0.005	0.070	0.013	-0.001	-0.007	-0.009	-0.003
C(5)	0.006	0.052	-0.004	-0.016	-0.029	-0.027	-0.024
N(6)	0.024	0.065	0.024	0.021	0.009	0.015	0.008
C(7)	0.007	0.017	0.006	0.023	0.017	0.029	0.000
C(8)	-0.014	-0.019	-0.013	0.016	0.018	0.031	-0.010
C(9)	0.014	0.009	0.022	0.054	0.065	0.075	0.031
C(10)	-0.007	0.004	0.005	0.028	0.041	0.047	0.012
C(11)	-0.032	-0.005	-0.022	-0.010	-0.004	-0.000	-0.023
C(12)	-0.031	-0.005	-0.028	-0.020	-0.023	-0.016	-0.035
C(13)	-0.017	0.054	0.002	-0.009	0.001	-0.008	-0.003
C(14)	0.066	0.136	0.062	0.039	0.015	0.018	0.033

2.4 Discussion

The bond distances and angles obtained in the analysis of 2,4-dimethyl-1,5-benzodiazepinium bromide suggest that the description of the structure in terms of the superposition of the four equivalent resonance forms (I - IV) is essentially correct.

The average of the six C-C distances within the benzene ring is 1.384 ± 0.020 Å, in reasonable agreement with that reported for crystalline benzene, 1.392 ± 0.004 Å (Cox et al., 1958) and gaseous benzene, 1.397 ± 0.001 Å (Stoicheff, 1954).

The C-N bonds within the seven membered ring fall into two groups. The C(3)-N(2) and C(5)-N(6) bond lengths of 1.32 ± 0.02 Å and 1.29 ± 0.02 Å respectively are shorter than the aromatic C-N distance of approximately 1.34 - 1.35 Å found in pyridine, pyrazine and related compounds. These rather short C-N bond lengths suggest contributions to the total structure from conjugation effects of the type (I - IV). The C(11)-N(2) and C(12)-N(6) bonds, which are adjacent to the benzene ring, are each 1.42 ± 0.02 Å in length; not as short as the C(3)-N(2) and C(5)-N(6) bonds, although considerably shorter than the single bond value of 1.46 - 1.50 Å found in hexamethylene-diamine (Brown, 1966) and in jamine (Karle and Karle, 1966). The C-N bond length of 1.42 Å is in close agreement with the values (1.42 ± 0.02 Å and 1.419 ± 0.008 Å) found for comparable bonds in the related molecules, 7-chloro-5-(2,4-dichlorophenyl)-4,5-

dihydro-1,4-dimethyl-3H-1,4-benzodiazepin-2-one (Karle and Karle, 1967) and 3,5-dihydro-3-methyl-4,1-benzothiazepin-2(1H)-one-4-oxide (Thomas et al., 1969) respectively.

The shape of the seven-membered ring in the cation is similar to that found in 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (Goldstein and Trueblood, 1967) with significant parallel trends in the averages of chemically equivalent bond angles within the seven-membered ring. The six atoms of the benzene ring are approximately planar (mean deviation, 0.01 Å) as are the atoms comprising the seven membered ring (mean deviation, 0.02 Å). These two rigid groups of atoms impose co-planarity on all the atoms in the molecule. The atoms comprising the molecule are indeed planar (mean deviation, 0.02 Å). The deviations of the atoms C(5), C(9), C(11), C(12) and C(14) from this plane may be real, but in any event are small.

Chapter 3

The Crystal and Molecular Structure of syn-3,7-Dibromo-*cis*,*cis*-cycloocta-1,5-diene

3.1 Introduction

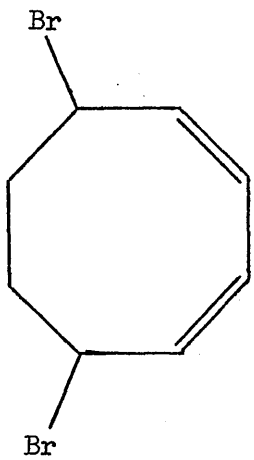
During the course of investigations into the synthesis of hydrocarbons isomeric with octa-1,7-diyne, (Zabkiewicz, 1965) attempts were made to prepare certain dibromocyclooctadiene derivatives by the allylic bromination of cycloocta-1,5-diene with N-bromosuccinimide. The oil obtained, on being chromatographed over alumina, yielded a solid ($C_8H_{10}Br_2$) in the later fractions.

The structure (I) proposed by Cope et al., (1950) for the oil obtained from an identical reaction was based on the characterisation of its i.r. and u.v. spectra. However it appears that structure (I) cannot be applied to this compound since attempts to prepare (I) by allylic bromination of cycloocta-1,3-diene proved unsuccessful (Cope and Estes, 1950).

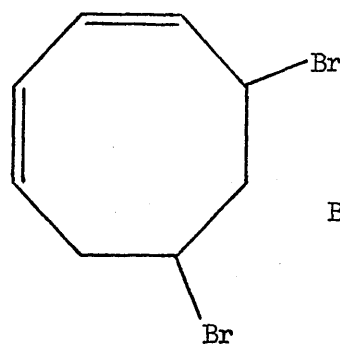
On the basis of a direct spectral comparison (i.r., u.v. and n.m.r.) between cycloocta-1,3-diene, 5-bromocycloocta-1,3-diene and the solid dibromocyclooctadiene, Zabkiewicz, (1965) was led to propose structure (II) for the dibromide. However the results of spin decoupling experiments on the compound ($C_8H_{10}Br_2$) isolated from the allylic bromination of cycloocta-1,5-diene are somewhat at variance with structure (II), (MacNicol, 1969).

In order to resolve the ambiguities concerning the structure of the compound $C_8H_{10}Br_2$, the present analysis was undertaken. This has shown that the correct formulation of the structure obtained by

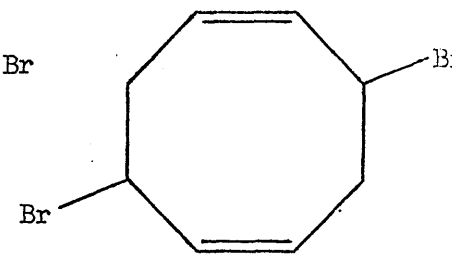
allylic bromination of cycloocta-1,5-diene is 3,7-dibromocycloocta-1,5-diene (III).



(I)



(II)



(III)

3.2 Experimental

Crystal Data

syn-3,7-dibromo-*cis*,*cis*-cycloocta-1,5-diene

$C_8H_{10}Br_2$ F.W. = 266.0

Orthorhombic, *a* = 19.64 Å, *b* = 19.36 Å, *c* = 4.78 Å

U = 1818 Å^3 F(000) = 1024 electrons

D_m = 1.94 g.cm.$^{-3}$ Z = 8 D_x = 1.944 g.cm.$^{-3}$

Space group: Fdd2 (C_{2v}^{19}, No. 43)

Linear absorption coefficient (Cu K_α, λ = 1.5418 Å) = 120 cm.$^{-1}$

The crystals used in this analysis were supplied by Dr. J.A. Zabkiewicz. They consisted of colourless needles elongated along the *c*-axis. Unit cell dimensions were obtained from rotation and Weissenberg photographs (Cu K_α radiation, λ = 1.5418 Å) taken about the *c*-axis. The space group was uniquely determined from the systematic absences in the diffracted spectra as Fdd2 (No. 43).

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the hk0,...,hk4 reciprocal lattice nets taken with Cu K_α radiation. The multiple film technique of Robertson, (1943) was used. The observed intensities were reduced to structure amplitudes by applying the appropriate Lorentz, polarisation and rotation factors (Tunell,

1939). 470 independent structure amplitudes (Table 3.4) were obtained, which represents 45 % of the data accessible to Cu K_α radiation. No absorption corrections were applied in the analysis.

The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

3.3 Solution and Refinement of the Structure

From the observed density and unit cell volume, the number of molecules present within the unit cell is eight. Since there are, however, sixteen equivalent positions in the space group Fdd2, the asymmetric unit of the structure is represented by one half molecule. The molecule therefore occupies a special position within the unit cell in which the two-fold axis of the molecule is co-incident with that due to the space group symmetry.

In the space group Fdd2, the equivalent positions are:-

(x, y, z), $(-x, -y, z)$, $(\frac{1}{4}-x, \frac{1}{4}+y, \frac{1}{4}+z)$, $(\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z)$;

together with those generated by the F-centred Bravais lattice given by:-

$(x, \frac{1}{2}+y, \frac{1}{2}+z)$, $(-x, \frac{1}{2}-y, \frac{1}{2}+z)$, $(\frac{1}{4}-x, \frac{3}{4}+y, \frac{3}{4}+z)$, $(\frac{1}{4}+x, \frac{3}{4}-y, \frac{3}{4}+z)$;

$(\frac{1}{2}+x, y, \frac{1}{2}+z)$, $(\frac{1}{2}-x, -y, \frac{1}{2}+z)$, $(\frac{3}{4}-x, \frac{1}{4}+y, \frac{3}{4}+z)$, $(\frac{3}{4}+x, \frac{1}{4}-y, \frac{3}{4}+z)$;

$(\frac{1}{2}+x, \frac{1}{2}+y, z)$, $(\frac{1}{2}-x, \frac{1}{2}-y, z)$, $(\frac{3}{4}-x, \frac{3}{4}+y, \frac{1}{4}+z)$, $(\frac{3}{4}+x, \frac{3}{4}-y, \frac{1}{4}+z)$.

A heavy atom situated in a general position will therefore give rise to the following set of vectors:-

$\pm (2x, -2y, 0)$ single weight,

$\pm (-2x, -2y, 0)$ single weight,

$\pm (\frac{1}{4}+2x, \frac{1}{4}, \frac{1}{4})$ single weight,

$\pm (\frac{1}{4}-2x, \frac{1}{4}, \frac{1}{4})$ single weight,

$\pm (\frac{1}{4}, \frac{1}{4}+2y, \frac{1}{4})$ single weight,

$\pm (\frac{1}{4}, \frac{1}{4}-2y, \frac{1}{4})$ single weight.

Thus in the three-dimensional Patterson summation there are six dominant peaks. Two are on the Harker section at w = 0 and four are on the Harker lines at v = $\frac{1}{4}$, w = $\frac{1}{4}$ and u = $\frac{1}{4}$, w = $\frac{1}{4}$ respectively. Therefore any peak from the Harker section, or any two peaks from each of the Harker lines will suffice to determine the x and y coordinates of the heavy atom.

The asymmetric unit of the three-dimensional Patterson function was calculated and interpreted on the basis of the analytical functions given. The values obtained for the coordinates of the bromine atom were:-

ATOM	X/a	Y/b	Z/c
Br(1)	0.2331	0.0708	0.0000

A set of structure factors, based on the coordinates of the bromine atom was calculated, and the calculated phase angles used in conjunction with the observed structure amplitudes to evaluate an electron density synthesis. The coordinates of the remaining non-hydrogen atoms in the structure were obtained from this initial electron density synthesis. Inclusion of the remaining four carbon atoms in the structure factor calculation reduced the R-factor from 0.33 based on bromine alone to 0.271. A further cycle of Fourier refinement reduced the R-factor to 0.267.

The structure was then refined in ten cycles of least-squares minimisation of the function $M = \sum w(|F_o| - |F_c|)^2$. D.R. Pollard's

least-squares program, (1968) was used in the initial stages of the refinement. Eachreciprocal lattice net was given an individual scale factor and each atom an individual isotropic temperature factor. The observations were all given unit weight. After three cycles of full matrix refinement the R-factor was reduced to 0.191. A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 5/|F_o|_{max}$ was then applied and a further cycle of least-squares refinement reduced the R-factor to 0.186.

The Glasgow S.F.L.S. program (Cruickshank and Smith, 1965) was then used to continue the refinement. On the assumption that the data were on the same relative scale, an anisotropic thermal parameter for the bromine atom and individual isotropic thermal parameters for the carbon atoms were refined together with an overall scale factor. As a result of allowing for the anisotropic vibration of the bromine atom, a further two cycles of refinement in which the block diagonal approximation to the normal matrix was applied reduced the R-factor to 0.142. Individual anisotropic thermal parameters were then assigned to all the atoms in the structure and a further four cycles of least-squares refinement reduced the R-factor to 0.112. The weighting scheme applied in the last six cycles of least-squares refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$$

where $p_1 = 5$, $p_2 = 0.01$ and $p_3 = 0.001$.

No shifts greater than 0.2σ in atomic coordinates or thermal parameters were observed in the final cycle of refinement. The course of the refinement is summarised in Table 3.1.

Tables 3.2 and 3.3 contain the final values of the fractional atomic coordinates and anisotropic temperature factors together with their estimated standard deviations. The observed and final calculated structure amplitudes are given in Table 3.4. Atomic coordinates in Angstroms referred to orthogonal axes defined by X parallel to $\underline{a}^*$, Y normal to $\underline{a}^*$ and $\underline{c}$ and Z parallel to $\underline{c}$ are given in Table 3.5. Tables 3.6 and 3.7 contain the bond lengths and interbond angles in the structure together with their estimated standard deviations. Table 3.8 lists the intermolecular contacts between the atoms which are less than 4 Å. In Table 3.9 the equations of certain mean molecular planes through portions of the molecule are given, together with the deviations of certain atoms from these planes. Estimated standard deviations, where quoted, are in units of the last decimal place of the quantity to which they refer.

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 3.1. A view of the molecule projected along a line in the mean planes through C(3), C(4), C(5)

and C(7); and through C(2), C(8), C(9) and C(10) is shown in Figs. 3.2 and 3.3 respectively. A view of the molecule projected along a line through the mid-points between C(2) and C(3) and C(7) and C(8) respectively is illustrated in Fig. 3.4. The general packing of the molecules in the unit cell, as projected on (001) is shown in Fig. 3.5.

TABLES AND DIAGRAMS

FIGURE 3.1

A molecular drawing illustrating the numbering of the non-hydrogen atoms of the molecule.

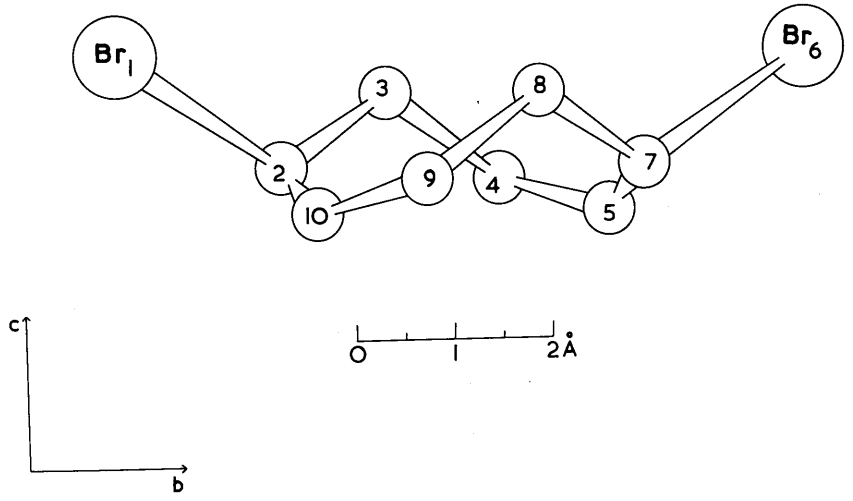

Br1
Br6
3
8
2
9
4
7
10
5
c
b
0
1
2Å

FIGURE 3.2

A drawing illustrating the molecule projected along a line in the mean molecular plane through C(3), C(4), C(5) and C(7).

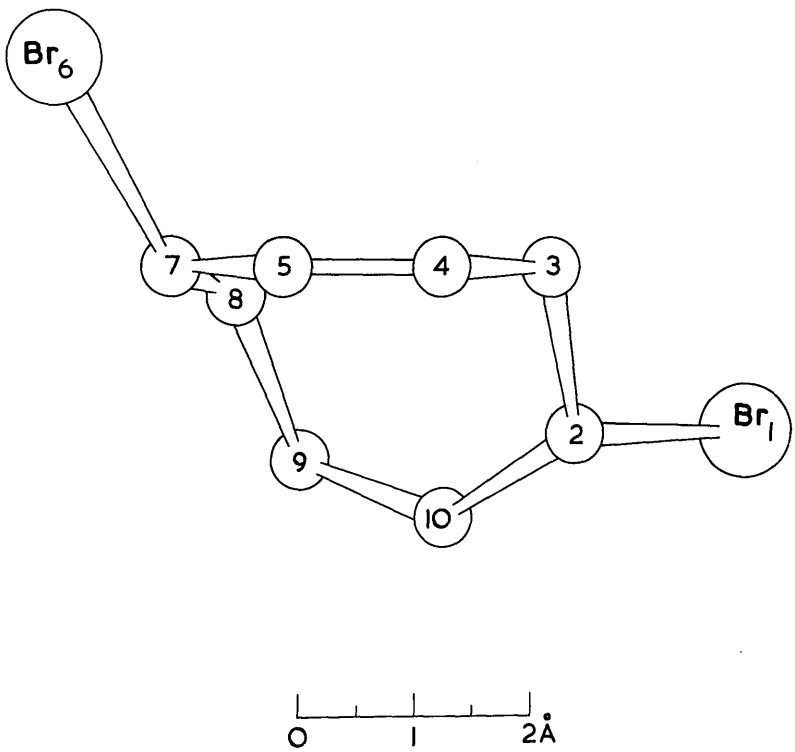

Br6
7
5
4
3
8
2
Br1
9
10
0
1
2Å

FIGURE 3.3

A drawing illustrating the molecule projected along a line in the mean molecular plane through C(2), C(8), C(9) and C(10).

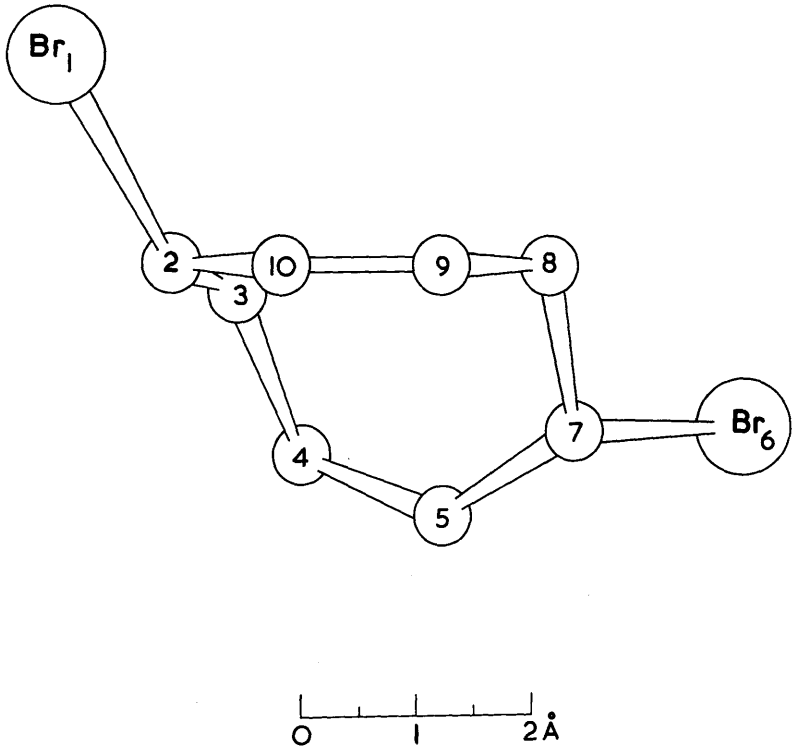

Br1
2
10
9
8
3
4
7
Br6
5
0
1
2 Å

FIGURE 3.4

A drawing illustrating the molecule projected along a line through the mid-points between C(2) and C(3) and C(7) and C(8) respectively.

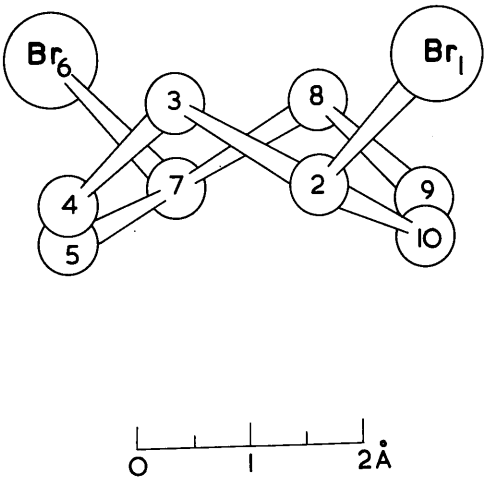

Br6
Br1
3
8
7
2
4
9
5
10
0
1
2Å

FIGURE 3.5

The molecular packing viewed down the c-axis.

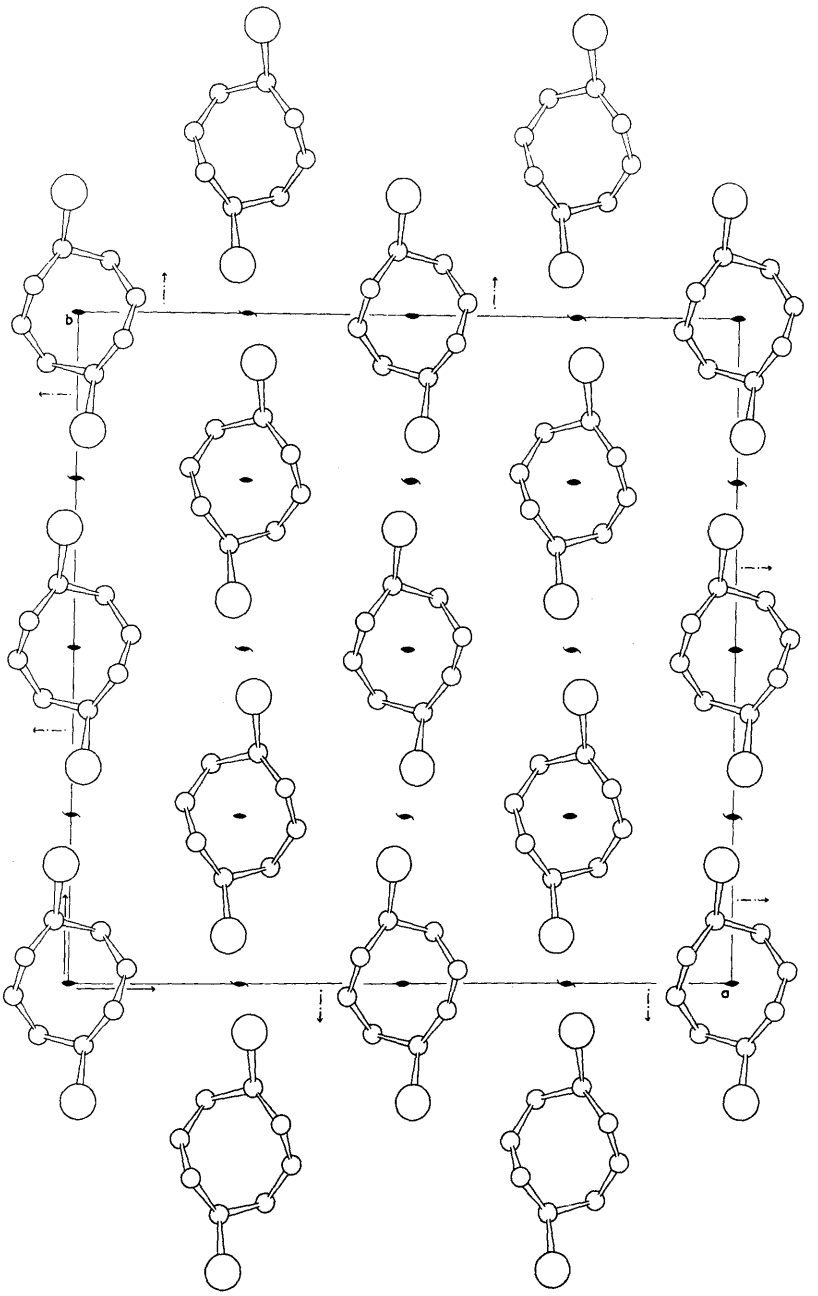

b
a

TABLE 3.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	Br	0.33
2	Br + 4 C	0.271
3	Br + 4 C	0.267

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layer scales, unit weights	0.207
2	"	0.192
3	"	0.191
4	As above, weighting scheme 1 applied	0.186
5	Block diagonal, Br anisotropic; 4 C isotropic, overall scale factor, weighting scheme 2 applied	0.148
6	"	0.142
7	As above, individual anisotropic temperature factors	0.126
8	"	0.117
9	"	0.113
10	"	0.112

TABLE 3.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
Br(1)	0.2339 ± 1	0.0719 ± 1	1.0000 ± 0
C(2)	0.2254 ± 10	0.1557 ± 10	0.7717 ± 59
C(3)	0.1836 ± 10	0.2096 ± 10	0.9209 ± 45
C(4)	0.1666 ± 10	0.2691 ± 12	0.7444 ± 73
C(5)	0.2045 ± 11	0.3263 ± 10	0.6776 ± 49

TABLE 3.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
Br(1)	0.0858	0.0697	0.0669	0.0034	0.0011	0.0003
	12	10	15	24	27	17
C(2)	0.0677	0.0607	0.0418	0.0195	-0.0061	-0.0055
	84	83	118	189	192	132
C(3)	0.0614	0.0701	0.0428	0.0205	-0.0217	-0.0307
	78	86	128	155	157	149
C(4)	0.0629	0.0836	0.0544	-0.0206	-0.0364	0.0044
	82	107	128	256	224	162
C(5)	0.0722	0.0606	0.0545	-0.0017	-0.0323	-0.0034
	102	88	182	164	184	151

TABLE 3.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES

H	K	L	F OBS	F CALC
4	0	0	900.7	902.6
8	0	0	135.6	156.7
12	0	0	73.7	71.8
16	0	0	9.9	12.1
20	0	0	76.3	35.9
24	0	0	12.9	24.0
2	2	0	168.1	151.8
2	4	0	114.2	99.0
2	6	0	249.4	275.2
2	8	0	36.5	30.6
2	10	0	66.1	68.1
2	12	0	33.4	23.3
2	14	0	174.3	184.9
2	16	0	42.6	43.9
2	18	0	15.7	8.5
2	20	0	11.2	10.9
2	22	0	31.9	41.4
2	24	0	8.7	9.1
4	2	0	157.6	149.3
4	4	0	184.4	169.7
4	6	0	80.2	62.4
4	8	0	277.2	273.0
4	10	0	79.3	85.7
4	12	0	148.7	145.4
4	14	0	11.4	18.3
4	16	0	55.5	52.4
4	18	0	11.3	6.4
4	20	0	42.2	45.0
4	22	0	7.1	3.6
6	2	0	293.3	289.7
6	4	0	191.0	197.4
6	6	0	193.7	197.8
6	8	0	99.1	89.3
6	10	0	59.3	65.5
6	12	0	103.4	95.8
6	14	0	113.2	102.2
6	16	0	70.8	67.6
6	18	0	22.6	19.9
6	20	0	15.1	16.2
6	22	0	20.0	27.0
8	2	0	219.9	208.9
8	4	0	98.0	86.8
8	6	0	91.7	82.4
8	8	0	134.3	122.4
8	10	0	126.0	116.2
8	12	0	85.9	83.5
8	14	0	31.7	19.3
8	16	0	43.6	39.9
8	18	0	38.3	38.2
8	20	0	20.9	25.5
8	22	0	5.1	5.0
10	2	0	105.8	108.9
10	4	0	203.3	208.4
10	6	0	150.6	144.9
10	8	0	57.8	57.8
10	10	0	26.2	24.8
10	12	0	102.4	107.5
10	14	0	58.3	59.0
10	16	0	39.4	43.8
10	18	0	10.0	12.1
10	20	0	7.6	10.7
10	22	0	7.2	9.2
12	2	0	156.9	173.9
12	4	0	19.0	15.4
12	6	0	40.8	43.9
12	8	0	72.9	31.5
12	10	0	119.9	138.4
12	12	0	9.6	5.9
12	14	0	9.7	20.4
12	16	0	7.3	10.4
12	18	0	33.8	42.4
12	20	0	7.4	8.1
14	2	0	3.1	4.7
14	4	0	129.3	141.6
14	6	0	54.5	42.4
14	8	0	19.1	20.0
14	10	0	8.3	14.1
14	12	0	77.6	80.2
14	14	0	15.1	20.8
14	16	0	30.0	33.2
14	20	0	11.7	12.0
16	2	0	115.9	118.0
16	4	0	10.6	12.5
16	6	0	38.2	40.7
16	8	0	4.8	1.3
16	10	0	80.8	93.1
16	12	0	12.7	17.0
16	14	0	20.1	23.1
16	16	0	47.0	58.0
16	18	0	16.6	17.2
18	8	0	26.4	26.6
18	10	0	12.3	12.9
18	12	0	30.6	33.1
18	14	0	8.5	11.5
18	16	0	17.3	20.8
20	2	0	48.1	55.7
20	6	0	32.6	31.2
20	8	0	10.7	15.4
20	10	0	24.7	33.7
22	2	0	10.6	13.9
22	4	0	23.4	27.1
22	6	0	11.1	20.0
22	8	0	14.3	16.1
0	4	0	112.1	96.0
0	8	0	365.3	344.1
0	12	0	140.7	152.9
0	16	0	49.0	42.3
0	20	0	53.3	58.5
0	24	0	2.0	2.6
1	1	1	222.2	204.2
1	3	1	288.2	281.0
1	5	1	244.6	224.9
1	7	1	24.7	16.2
1	9	1	160.6	171.4
1	11	1	133.7	137.1
1	13	1	14.7	6.6
1	15	1	45.1	51.6
1	17	1	67.1	61.4
1	19	1	30.3	28.1
1	21	1	5.5	6.9
1	23	1	12.6	19.6
3	1	1	234.6	224.9
3	3	1	302.0	284.9
3	5	1	249.3	229.5
3	7	1	147.3	121.7
3	9	1	138.8	141.9
3	11	1	128.8	133.5
3	13	1	67.8	58.7
3	15	1	66.4	62.4
3	17	1	73.9	76.1
3	19	1	41.2	38.0
3	23	1	15.4	20.8
5	1	1	168.7	179.1
5	3	1	249.8	236.4
5	5	1	162.0	148.4
5	7	1	91.8	91.6
5	9	1	112.0	122.4
5	11	1	134.1	116.6
5	13	1	60.4	50.3
5	15	1	49.4	43.1
5	17	1	42.6	38.6
5	19	1	23.4	23.3
5	21	1	17.3	22.4
5	23	1	3.8	10.1
7	1	1	121.6	126.0
7	3	1	177.1	179.6
7	5	1	144.7	145.8
7	7	1	108.7	124.0
7	9	1	101.5	107.1
7	11	1	132.2	126.5
7	13	1	76.5	69.8
7	15	1	37.9	46.1
7	17	1	46.3	48.9
7	19	1	26.7	30.9
7	21	1	9.8	17.2
9	1	1	149.2	173.5
9	3	1	135.9	145.7
9	5	1	114.6	124.5
9	7	1	111.1	122.3
9	9	1	102.1	95.7
9	11	1	61.0	62.9
9	13	1	69.7	66.3
9	15	1	46.7	45.2
9	17	1	28.2	27.1
9	19	1	19.1	27.3
9	21	1	11.7	19.0
11	1	1	103.6	124.6
11	3	1	69.0	71.4
11	5	1	66.6	83.6
11	7	1	70.4	82.0
11	9	1	60.9	66.0
11	11	1	41.4	49.0
11	13	1	46.6	54.9
11	15	1	28.4	32.4
11	17	1	14.3	18.8
11	19	1	16.7	21.9
11	21	1	11.2	15.6
13	1	1	90.6	111.7
13	3	1	35.4	42.0
13	5	1	84.4	100.4
13	7	1	76.2	102.0
13	9	1	49.2	66.1
13	11	1	22.0	33.1
13	13	1	42.3	60.2
13	15	1	12.9	38.1
13	19	1	8.7	18.4
15	1	1	66.7	78.8
15	3	1	35.0	32.5
15	5	1	39.7	46.3
15	7	1	59.4	70.4
15	9	1	36.5	42.6
15	13	1	25.5	33.5
15	15	1	16.8	29.3
15	17	1	4.6	5.4
17	1	1	57.0	69.4
17	3	1	15.6	15.0
17	5	1	28.4	40.3
17	7	1	46.4	59.5
17	9	1	12.4	19.9
17	11	1	5.9	15.1
17	13	1	28.4	29.4
17	15	1	13.9	21.7
19	1	1	27.2	39.7
19	3	1	16.4	27.4
19	5	1	20.2	28.1
19	7	1	15.6	44.2
19	9	1	13.7	21.8
19	13	1	18.8	19.9
19	15	1	15.2	21.6
21	1	1	21.8	31.2
21	7	1	15.1	25.7
21	9	1	11.2	15.7
21	11	1	5.5	11.1
23	1	1	10.1	18.9
2	0	2	239.3	234.6
2	2	2	206.6	223.4
2	4	2	103.1	98.7
2	6	2	33.7	37.2
2	8	2	3.7	3.2
2	10	2	19.7	24.1
2	12	2	81.9	76.1
2	14	2	58.0	66.4
2	16	2	79.7	64.3
2	18	2	19.6	230.1
2	20	2	25.0	23.1
2	22	2	80.0	72.4
4	0	2	9.7	5.2
4	2	2	83.4	80.2
4	4	2	80.7	90.0
4	6	2	226.3	253.3
4	8	2	79.2	70.3
4	10	2	23.0	17.3
4	12	2	50.8	43.5
4	14	2	122.4	101.6
4	16	2	27.8	21.0
4	18	2	28.6	17.9
4	20	2	7.7	10.1
4	22	2	30.3	17.6
6	2	2	121.2	125.5
6	6	2	80.2	74.8
6	8	2	139.5	129.6
6	10	2	114.7	93.6
6	12	2	81.8	69.4
6	16	2	51.7	39.5
6	18	2	40.9	35.1
6	20	2	54.0	36.6
6	22	2	14.3	12.7
8	2	2	86.9	98.3
8	4	2	148.6	189.6
8	6	2	131.2	127.3
8	8	2	61.6	55.2
8	10	2	23.3	28.0
8	12	2	57.4	42.6
8	14	2	52.0	53.3
8	16	2	57.5	38.5
8	18	2	7.5	6.9
8	20	2	10.0	7.3
8	22	2	12.2	9.5
10	2	2	99.3	102.7
10	4	2	36.2	37.8
10	6	2	46.7	49.2
10	8	2	76.5	72.8
10	10	2	119.1	107.7
10	12	2	48.0	45.5
10	14	2	10.6	10.6
10	16	2	26.1	20.1
10	18	2	53.6	40.5
10	20	2	21.7	17.1
12	2	2	49.3	38.2
12	4	2	151.5	153.7
12	6	2	32.0	23.6
12	8	2	63.4	58.4
12	10	2	3.8	7.9
12	12	2	67.9	49.3
12	14	2	36.1	16.9
12	16	2	49.2	33.6
12	18	2	2.7	4.1
12	20	2	6.9	4.2
14	2	2	86.7	77.6
14	4	2	15.6	12.5
14	6	2	47.7	47.9
14	8	2	21.7	21.5
14	10	2	70.4	61.1
14	12	2	9.6	9.2
14	14	2	5.8	1.2
14	18	2	37.8	29.7
16	2	2	17.3	18.0
16	4	2	90.1	89.8
16	6	2	5.3	9.9
16	8	2	51.0	46.7
16	10	2	8.9	7.2
16	12	2	45.5	38.7
16	14	2	2.9	3.8
16	16	2	26.9	24.8
18	2	2	42.8	44.1
18	4	2	9.6	6.0
18	6	2	25.2	27.6
18	8	2	16.7	12.9
18	10	2	40.2	34.0
20	2	2	14.1	15.0
20	4	2	39.4	39.9
20	6	2	14.1	16.2
20	8	2	12.1	17.8
20	12	2	12.3	14.7
22	2	2	17.7	19.8
22	6	2	5.6	8.9
22	8	2	12.7	16.2
0	2	2	251.1	256.0
0	6	2	285.6	280.2
0	10	2	12.7	15.5
0	14	2	136.1	124.8
0	18	2	42.7	31.4
0	22	2	45.9	27.7
1	1	3	64.2	72.3
1	3	3	116.9	129.4
1	5	3	70.1	84.1
1	7	3	14.9	13.0
1	9	3	102.3	93.2
1	11	3	97.8	86.1
1	13	3	28.2	19.3
1	15	3	30.6	20.9
1	17	3	44.1	35.1
1	19	3	30.3	23.7
3	1	3	54.3	79.0
3	3	3	131.3	138.4
3	5	3	110.1	119.5
3	7	3	42.5	52.7
3	9	3	64.2	58.2
3	11	3	77.4	67.1
3	13	3	34.7	27.7
3	15	3	28.2	21.9
3	17	3	49.2	31.5
3	19	3	29.6	20.1
3	21	3	7.7	5.3
5	1	3	44.5	64.9
5	3	3	115.1	107.5
5	5	3	70.5	70.6
5	7	3	45.3	49.9
5	9	3	24.5	27.9
5	11	3	63.1	62.6
5	13	3	37.6	27.7
5	15	3	41.9	34.9
5	17	3	33.9	29.4
5	19	3	23.8	19.4
5	21	3	11.8	9.4
7	1	3	73.2	77.1
7	3	3	73.2	81.3
7	5	3	92.7	97.0
7	7	3	72.3	74.3
7	9	3	61.7	50.8
7	11	3	50.8	48.4
7	13	3	44.9	34.3
7	15	3	27.3	25.6
7	17	3	32.3	23.7
7	19	3	14.9	13.7
9	1	3	54.9	69.6
9	3	3	85.8	77.0
9	5	3	80.0	78.9
9	7	3	65.8	64.5
9	9	3	34.3	35.0
9	11	3	28.5	25.4
9	15	3	43.2	34.1
9	13	3	37.0	36.3
9	17	3	15.9	14.3
9	19	3	15.1	12.2
11	1	3	72.4	69.8
11	3	3	30.0	31.3
11	5	3	34.8	40.7
11	7	3	59.7	57.7
11	9	3	40.3	33.5
11	11	3	21.5	21.5
11	13	3	36.4	30.2
11	15	3	24.0	22.8
11	17	3	13.9	15.8
13	1	3	54.4	61.4
13	3	3	30.5	29.2
13	5	3	40.2	45.5
13	7	3	65.2	57.1
13	9	3	28.0	31.7
13	11	3	14.1	12.5
13	13	3	20.1	17.3
13	15	3	4.3	4.1
15	1	3	37.6	36.6
15	3	3	4.7	3.2
15	5	3	19.8	23.1
15	7	3	36.3	35.8
15	9	3	27.3	22.3
15	11	3	9.0	12.2
15	13	3	22.0	23.4
15	15	3	17.3	17.0
17	1	3	44.7	45.6
17	3	3	8.9	9.1
17	5	3	21.2	20.7
17	7	3	24.7	31.1
17	9	3	14.7	18.8
17	11	3	6.7	8.1
17	13	3	8.8	13.4
19	1	3	15.2	19.2
19	5	3	9.0	12.7
19	7	3	15.4	20.1
19	9	3	12.3	16.7
21	1	3	8.3	14.7
21	3	3	6.8	10.3
21	5	3	10.8	15.8
4	0	4	97.8	104.6
8	0	4	55.5	69.5
12	0	4	32.1	26.0
16	0	4	16.0	11.3
2	2	4	52.2	66.0
2	4	4	24.7	25.3
2	6	4	87.4	82.5
2	8	4	9.9	12.7
2	10	4	37.4	24.7
2	12	4	12.6	5.9
2	14	4	52.0	46.5
2	16	4	13.3	8.0
2	18	4	10.0	5.5
4	2	4	36.3	37.0
4	4	4	27.6	31.3
4	6	4	11.1	10.1
4	8	4	62.6	69.7
4	10	4	47.3	39.1
4	12	4	49.4	36.4
4	14	4	11.0	9.0
4	16	4	12.5	10.0
6	4	4	21.3	14.4
6	6	4	50.2	51.7
6	8	4	53.3	46.6
6	6	4	61.4	51.9
6	8	4	19.9	17.0
6	10	4	15.1	10.8
6	12	4	31.4	24.7
6	14	4	54.9	34.0
6	16	4	16.2	13.4
8	2	4	56.1	62.3
8	4	4	17.0	16.5
8	6	4	26.9	24.3
8	8	4	47.6	44.4
8	10	4	37.6	39.1
8	12	4	24.7	19.3
8	14	4	11.4	9.3
8	16	4	11.5	9.1
10	2	4	14.9	19.3
10	4	4	40.3	45.6
10	6	4	31.0	30.1
10	8	4	18.4	20.1
10	12	4	33.5	30.1
10	14	4	15.3	16.4
10	16	4	11.3	15.2
12	2	4	49.7	52.1
12	4	4	8.2	3.2
12	6	4	18.2	21.6
12	8	4	10.1	13.3
12	10	4	15.9	25.3
12	12	4	6.4	9.1
14	4	4	35.5	39.9
14	12	4	17.1	19.0
16	2	4	25.6	28.9
16	4	4	8.9	1.4
16	10	4	15.9	24.4
18	4	4	19.5	25.4
18	6	4	25.2	29.3
18	8	4	64.4	70.5
18	12	4	60.8	45.5
18	16	4	14.6	14.7

TABLE 3.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X	Y	Z
Br(1)	4.594 ± 2	1.393 ± 2	4.780 ± 0
C(2)	4.425 ± 19	3.015 ± 20	3.689 ± 28
C(3)	3.605 ± 20	4.059 ± 20	4.402 ± 22
C(4)	3.271 ± 19	5.212 ± 24	3.558 ± 35
C(5)	4.015 ± 22	6.318 ± 19	3.239 ± 23

TABLE 3.6

BOND LENGTHS AND E.S.D.S.

Br(1)- C(2)	1.963 ± 23 Å	C(5) - C(7)	1.491 ± 29 Å
C(2) - C(3)	1.507 ± 30	Br(6)- C(7)	1.963 ± 23
C(2) - C(10)	1.491 ± 29	C(7) - C(8)	1.507 ± 30
C(3) - C(4)	1.467 ± 35	C(8) - C(9)	1.467 ± 35
C(4) - C(5)	1.371 ± 30	C(9) - C(10)	1.371 ± 31

TABLE 3.7

INTERBOND ANGLES AND E.S.D.S.

Br(1)- C(2) - C(3)	110.9 ± 17°	C(5) - C(7) - Br(6)	106.4 ± 13°
Br(1)- C(2) - C(10)	106.4 ± 13	C(5) - C(7) - C(8)	118.9 ± 17
C(3) - C(2) - C(10)	118.9 ± 17	Br(6)- C(7) - C(8)	110.9 ± 17
C(2) - C(3) - C(4)	113.3 ± 21	C(7) - C(8) - C(9)	113.3 ± 21
C(3) - C(4) - C(5)	130.2 ± 20	C(8) - C(9) - C(10)	130.2 ± 20
C(4) - C(5) - C(7)	128.3 ± 21	C(2) - C(10)- C(9)	128.3 ± 21

TABLE 3.8

INTERMOLECULAR CONTACTS BELOW 4 Å

Br(1)....Br(1)	iv	3.72 Å	Br(1)....C(5)	v	3.98 Å
Br(1)....C(4)	ii	3.92	Br(1)....C(4)	i	4.00
Br(1)....C(4)	iii	3.95			

Roman numerals refer to the transformations of the fractional coordinates given in Table 3.2.

i $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$; iv $\frac{1}{2} - x, -y, \frac{1}{2} + z$;

ii $\frac{1}{4} - x, -\frac{1}{4} + y, \frac{3}{4} + z$; v $\frac{1}{2} - x, \frac{1}{2} - y, 1 + z$;

iii $\frac{1}{4} - x, -\frac{1}{4} + y, -\frac{1}{4} + z$;

(C) DEVIATIONS FROM PLANES (Å)

PLANE NO. ATOM	1	2
Br(1)	1.344	-1.705
C(2)	1.374	0.001
C(3)	0.001	0.238
C(4)	-0.003	1.583
C(5)	0.003	2.084
Br(6)	-1.705	1.344
C(7)	-0.001	1.374
C(8)	0.238	0.001
C(9)	1.583	-0.003
C(10)	2.084	0.003

(D) DIHEDRAL ANGLES

PLANE A	PLANE B	∠ AB
1	2	74.2°

3.4 Discussion

Six crystal structure analyses of cycloocta-1,5-diene metal complexes have been reported; viz., di-μ-chloro-bis-(triphenyl-phosphite)-(cycloocta-1,5-diene)-di-rhodium(I), Coetzer and Gafner, (1970), cycloocta-1,5-diene-rhodium(I) chloride, Ibers and Snyder, (1962), cycloocta-1,5-diene-copper(I) chloride, Baird and van den Hende, (1963), cycloocta-1,5-diene-duroquinone-nickel(0), Glick and Dahl, (1965), bis-cycloocta-1,5-diene-nickel(0), Dierks and Dietrich, (1965) and π-cyclooctenyl-π-cycloocta-1,5-diene-cobalt(0), Koda et al., (1971). In all six cases, the cyclooctadiene molecule occurs in the boat or tub conformation with idealised symmetry mm2 rather than the alternative chair form with idealised symmetry 2/m. In each case, both double bonds are π - bonded to a transition metal atom and since this is only possible in the boat form, these results do not apply, mutatis mutandis, to the conformation of the uncomplexed diene.

Roberts, (1950) has shown from dipole moment measurements that 1,6-dichlorocycloocta-1,5-diene exists predominantly in the boat form and, more recently, an electron diffraction study of gaseous cycloocta-1,5-diene (Hedberg and Hedberg, 1964) has shown that the boat form predominates. On the other hand, dibenzocycloocta-1,5-diene is reported to possess the chair conformation in the crystalline state (Baker et al., 1945). However the ^{1}H n.m.r.

spectrum of 1,2:5,6-dibenzocycloocta-1,5-dien-3-one is more readily reconciled with a twist-tub than a chair conformation (Davies and Graham, 1968).

In the present analysis the conformation adopted by the 3,7-dibromocycloocta-1,5-diene molecule is that of a twist-tub with a dihedral angle of approximately 74° between the mean molecular planes containing the olefinic double bonds. The observed preference for the tub and twist-tub conformations in the complexed and uncomplexed dienes respectively may indicate that an energetically inexpensive pseudo-rotation, which would interconvert mirror image twist-tubs, is possible.

Although the analysis was undertaken to determine the stereochemistry and conformation of the dibromide obtained by Zabkiewicz, the results obtained allow something to be said concerning the geometry of the cycloocta-1,5-diene ring. The distinctive structural feature common to all cycloocta-1,5-dienes studied, except where the magnitude of errors does not support such conclusions, is that $HC=CH-CH_2$ angles adjacent to the double bond are considerably and consistently larger than those normally encountered in other unsaturated molecules. Examination of the angles given in Table ii indicates that the average values of the adjacent $HC=CH-CH_2$ and non-adjacent $HC-CH_2-CH_2$ angles in free cycloocta-1,5-diene are in good agreement with those found in 3,7-dibromocycloocta-1,5-diene.

The two approximately equal single bonds adjacent to the olefinic bond (1.47 ± 0.04 Å, 1.49 ± 0.03 Å) have an average value of 1.48 Å which is in reasonable agreement with the average value of 1.502 Å found in free cycloocta-1,5-diene. The value of 1.51 Å for the single bond non-adjacent to the C=C double bond, is shorter than that found in the other analysis although, in view of the errors present, this is probably not significant. The olefinic bond length of 1.37 ± 0.03 Å is in reasonable agreement with that found in cycloocta-1,5-diene, viz., 1.34 Å.

The bond lengths and interbond angles of the cycloocta-1,5-diene ring are given in Tables i and ii respectively, together with representative values taken from the literature for comparison.

Table i

(Bond Lengths)

Type*	cycloocta-1,5-diene**	3,7-dibromocycloocta-1,5-diene
C_1-C_2	1.341 Å	1.37 ± 0.03 Å
C_1-C_8	1.502 (av.)	1.47 ± 0.04
C_2-C_3		1.49 ± 0.03
C_3-C_4	1.554	1.51 ± 0.03

Table ii

(Interbond Angles)

Type*	cycloocta-1,5-diene**	3,7-dibromocycloocta-1,5-diene
C_1-C_2-C_3	127.8° (av.)	128.3 ± 2.1°
C_4-C_5-C_6		130.2 ± 2.0
C_2-C_3-C_4	116.8 (av.)	118.9 ± 1.7
C_3-C_4-C_5		113.3 ± 2.1

* The subscripted chemical designations are related to the crystallographic notation as follows:-

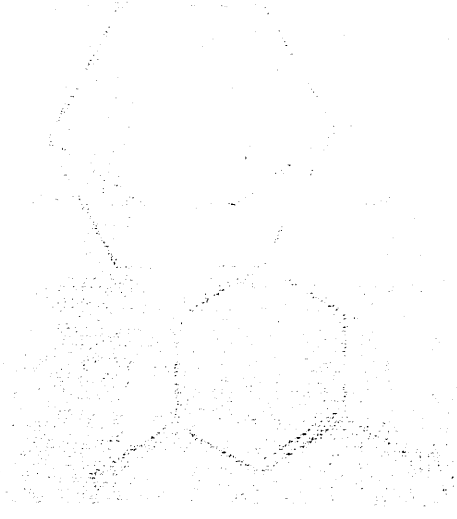
C_1 = C(4) C_3 = C(7) C_5 = C(9) C_7 = C(2)

C_2 = C(5) C_4 = C(8) C_6 = C(10) C_8 = C(3)

** Hedberg and Hedberg, (1964)

Chapter 4

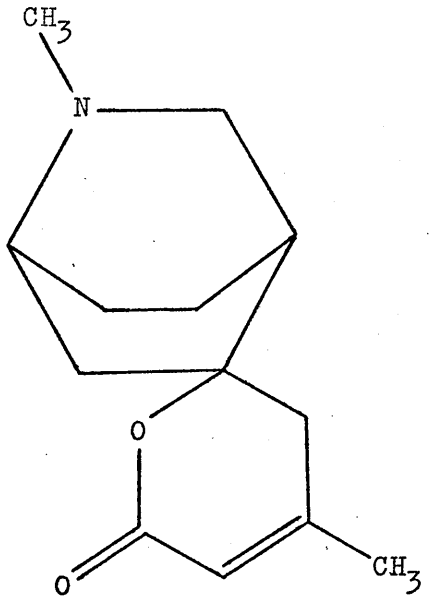
The Crystal and Molecular Structure of Dioscorine Methobromide



4.1 Introduction

The alkaloid, dioscorine, was first isolated by Boorsma, (1894) from the tubers of Dioscorea hirsuta, Blume, found in Java. The alkaloid was obtained in a crystalline condition by Schutte, (1897) who also prepared several crystalline salts. In 1937, Leyva and Gutierrez isolated an alkaloid from the tubers of Dioscorea hispida, Dennst., found in the Philippine islands, which was ultimately shown to be identical with dioscorine (Pinder, 1951).

On the basis of extensive degradative studies by Pinder and co-workers, (1952 - 1963) the structure shown below was finally postulated for the alkaloid.



(I)

In 1964, a synthesis of dioscorine by Page and Pinder gave a product identical in all respects with the natural alkaloid.

4.2 Experimental

Crystal Data

dioscorine methobromide

$C_{14}H_{22}BrNO_2$ F.W. = 316.2

Monoclinic, $\underline{a}$ = 9.77 Å, $\underline{b}$ = 9.71 Å, $\underline{c}$ = 16.44 Å,

β = 106.6°

U = 1494 Å^3 F(000) = 656 electrons

D_m = 1.43 g.cm.$^{-3}$ Z = 4 D_x = 1.406 g.cm.$^{-3}$

Space group: C2 (C_2^3, No. 5)

Linear absorption coefficient (Cu K_α, λ = 1.5418 Å) = 41 cm.$^{-1}$

The crystals used in this analysis were supplied by Professor A.R. Pinder. They consisted of colourless plates. Unit cell dimensions were obtained from rotation and Weissenberg photographs (Cu K_α radiation, λ = 1.5418 Å) taken about the $\underline{b}$-axis. The systematic absences present in the diffracted spectra are characteristic of the space groups C2 (No. 5), Cm (No. 8) and C2/m (No. 12). Since the compound is optically active, the space group is C2 (No. 5).

The intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the h0l,...,h8l reciprocal lattice nets, taken with Cu K_α radiation. The multiple film technique of Robertson, (1943) was used. The observed

intensities were reduced to structure amplitudes by applying the appropriate Lorentz, polarisation and rotation factors (Tunell, 1939). 1481 independent structure amplitudes (Table 4.4) were obtained, which represents 43 % of the data accessible to Cu K_α radiation. No absorption corrections were applied in this analysis.

The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale factors were determined by least-squares refinement.

4.3 Solution and Refinement of the Structure

In the space group C2 the equivalent positions are:-

$$(x, y, z), (-x, y, -z);$$

together with those generated by the C-centred Bravais lattice and given by:-

$$(\tfrac{1}{2}+x, \tfrac{1}{2}+y, z), (\tfrac{1}{2}-x, \tfrac{1}{2}+y, -z).$$

A heavy atom situated in a general position will therefore give rise to a single vector set:-

$$\pm (2x, 0, 2z),$$

on the Harker section at v = 0.

The asymmetric unit of the three-dimensional Patterson function was calculated and interpreted. The largest peak present on the Harker section at v = 0 was chosen as the heavy atom vector. The values obtained for the coordinates of the bromide ion were:-

ATOM	X/a	Y/b	Z/c
Br(1)	0.2827	0.5000	0.1310

A set of structure factors, based on the coordinates of the bromide ion was calculated, and the calculated phase angles used in conjunction with the observed structure amplitudes to evaluate an electron density synthesis. The coordinates of all the remaining non-hydrogen atoms in the structure were obtained from this initial electron density synthesis. The different chemical species present in the structure were differentiated on the basis of peak height and

knowledge of the chemical structure. Inclusion of the remaining seventeen atoms (2 oxygen, 1 nitrogen and 14 carbon) in the subsequent structure factor calculation reduced the R-factor from 0.46, based on the bromide ion alone, to 0.356. A further cycle of Fourier refinement reduced the R-factor to 0.334.

The structure was then refined in ten cycles of least-squares minimisation of the function $M = \Sigma w(|F_o| - |F_c|)^2$. D.R. Pollard's least-squares program, (1968) was used in the initial stages of the refinement. Three positional and one isotropic thermal parameters for each atom and an individual scale factor for each reciprocal lattice net were refined. Four consecutive cycles of refinement, in which the observations were given unit weights and the full matrix of the normal equations was evaluated, reduced the R-factor to 0.220. A weighting scheme of the form

$$w = 1/(p_1 + |F_o| + p_2|F_o|^2)$$

where $p_1 = 2|F_o|_{min}$ and $p_2 = 2/|F_o|_{max}$ was then applied and a further cycle of least-squares refinement reduced the R-factor to 0.203.

On the assumption that the data were now on the same relative scale, the isotropic temperature factors were replaced by six anisotropic temperature factors and the individual layer scale factors by one overall scale factor. The refinement was continued using the Glasgow S.F.L.S. program (Cruickshank and Smith, 1965). Convergence was achieved in a further four cycles of refinement in

which the block diagonal approximation to the matrix of the normal equations was used. The R-factor at the conclusion of the analysis was 0.165. The weighting scheme which was applied in the last four cycles of refinement was of the form

$$w = (1 - \exp -p_1 \sin^2\theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$$

where $p_1 = 5$, $p_2 = 0.01$ and $p_3 = 0.001$ respectively.

In the final cycle of refinement the shifts in both positional and thermal parameters were less than one third of the corresponding standard deviations. The course of the analysis is summarised in Table 4.1.

Tables 4.2 and 4.3 contain the final values of the fractional atomic coordinates and anisotropic temperature factors together with their estimated standard deviations. The observed and final calculated structure amplitudes are given in Table 4.4. Atomic coordinates in Angstroms referred to orthogonal axes defined by X' parallel to $\underline{a}^*$, Y normal to $\underline{a}^*$ and $\underline{c}$ and Z' parallel to $\underline{c}$ are given in Table 4.5. Tables 4.6 and 4.7 contain the bond lengths and interbond angles in the structure together with their estimated standard deviations. Table 4.8 lists all intermolecular contacts between atoms which are less than 4 Å. In Table 4.9 the equations of the mean planes through portions of the molecule are given, together with the deviations of certain atoms from these planes. Estimated standard deviations, where quoted, are in units of the

last decimal place of the quantity to which they refer.

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 4.1. The lactone ring projected along a line in the mean plane through O(2), O(3), C(11), C(12) and C(13) is shown in Fig. 4.2. The general packing of the molecules in the unit cell, as projected on (010) is shown in Fig. 4.3.

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A molecular drawing illustrating the numbering of the atoms in the structure is shown in Fig. 4.1. The lactone ring projected along a line in the mean plane through O(2), O(3), C(11), C(12) and C(13) is shown in Fig. 4.2. The general packing of the molecules in the unit cell, as projected on (010) is shown in Fig. 4.3.

TABLES AND DIAGRAMS

FIGURE 4.1

A molecular drawing illustrating the numbering of the non-hydrogen atoms in the structure.

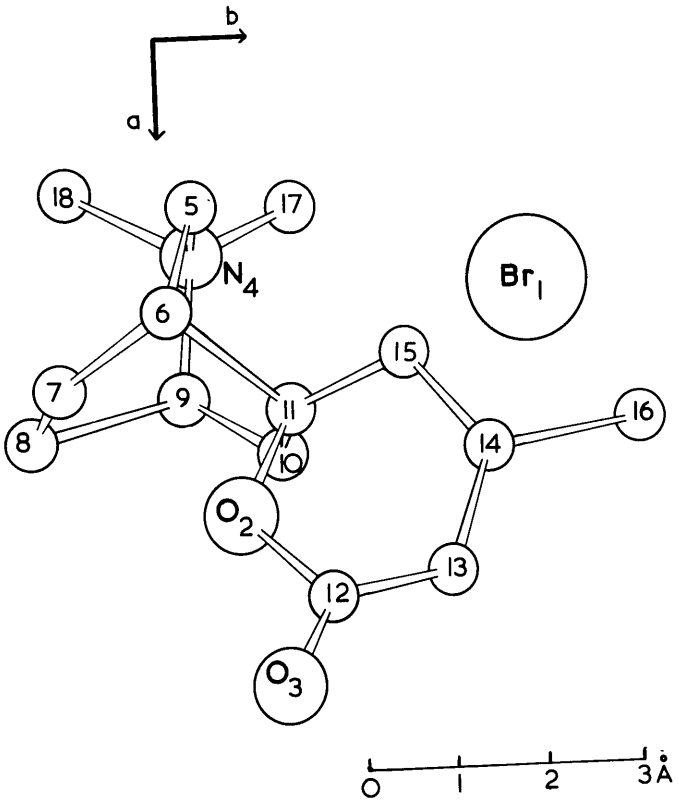
b
a
18
5
17
N4
Br1
6
15
7
9
11
16
8
14
10
O2
13
12
O3
0
1
2
3Å

FIGURE 4.2

A molecular drawing illustrating the lactone ring projected along a line in the mean molecular plane through O(2), O(3), C(11), C(12) and C(13).

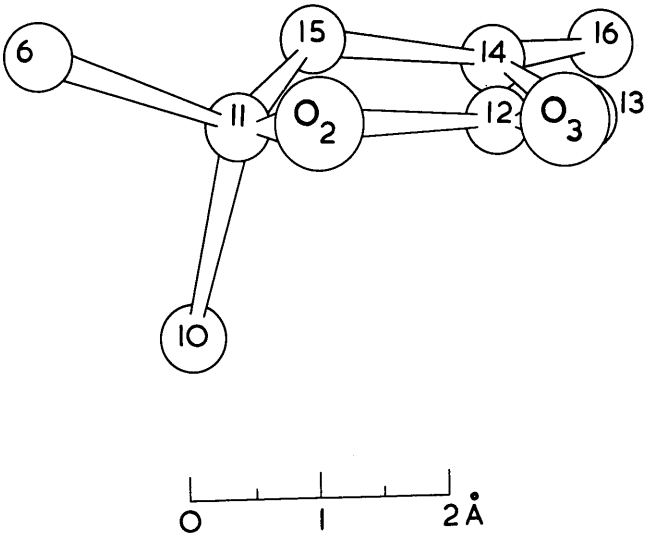
6
15
16
14
11
O2
12
O3
13
10
0
1
2 Å

FIGURE 4.3

The packing of the molecules as projected on (010).

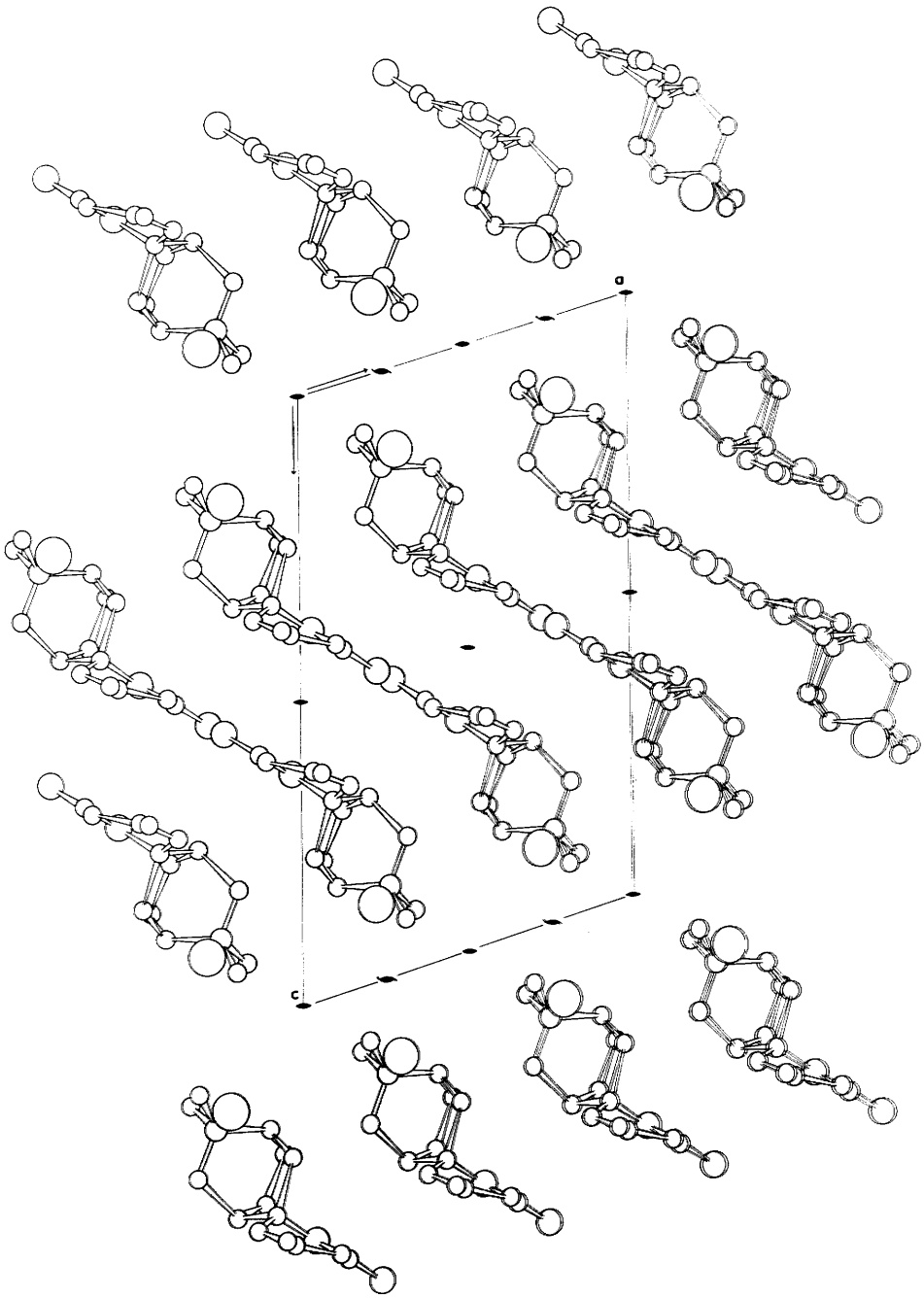
a
c

TABLE 4.1

COURSE OF THE ANALYSIS

1. Fourier Refinement

S.F. Cycle No.	Atoms Included	R
1	Br	0.46
2	Br + 14 C + N + 2 O	0.356
3	Br + 14 C + N + 2 O	0.334

2. Least-squares Refinement

S.F.L.S. Cycle No.	Comments	R
1	Full matrix, individual isotropic temperature factors, layer scales, unit weights	0.257
2	"	0.234
3	"	0.224
4	"	0.220
5	As above, weighting scheme 1 applied	0.206
6	"	0.203
7	Block diagonal, individual anisotropic temperature factors, overall scale factor, weighting scheme 2 applied	0.178
8	"	0.168
9	"	0.166
10	"	0.165

TABLE 4.2

FRACTIONAL COORDINATES AND E.S.D.S.

ATOM	X/a	Y/b	Z/c
Br(1)	0.2844 ± 2	0.5121 ± 0	0.1309 ± 1
O(2)	0.5332 ± 17	0.0754 ± 18	0.3887 ± 9
O(3)	0.7290 ± 19	0.1211 ± 26	0.4903 ± 10
N(4)	0.2426 ± 18	0.0307 ± 19	0.1519 ± 10
C(5)	0.1889 ± 22	0.0345 ± 50	0.2243 ± 15
C(6)	0.3036 ± 22	0.0007 ± 35	0.3089 ± 11
C(7)	0.3851 ± 24	-0.1200 ± 49	0.3029 ± 12
C(8)	0.4426 ± 16	-0.1290 ± 22	0.2294 ± 10
C(9)	0.3991 ± 21	0.0159 ± 33	0.1806 ± 14
C(10)	0.4663 ± 21	0.1222 ± 27	0.2397 ± 16
C(11)	0.4157 ± 18	0.1363 ± 27	0.3254 ± 13
C(12)	0.6294 ± 19	0.1745 ± 24	0.4374 ± 13
C(13)	0.6078 ± 17	0.3123 ± 32	0.4240 ± 13
C(14)	0.4697 ± 18	0.3608 ± 23	0.3834 ± 12
C(15)	0.3614 ± 25	0.2673 ± 28	0.3399 ± 14
C(16)	0.4461 ± 23	0.5302 ± 28	0.3754 ± 12
C(17)	0.1933 ± 46	0.1453 ± 46	0.0885 ± 25
C(18)	0.1672 ± 18	-0.1057 ± 25	0.1002 ± 11

TABLE 4.3

ANISOTROPIC TEMPERATURE FACTORS AND E.S.D.S.

ATOM	U11	U22	U33	2U23	2U31	2U12
Br(1)	0.0777 11	0.0854 16	0.0744 11	0.0009 29	0.0121 17	-0.0017 29
O(2)	0.0829 88	0.0509 88	0.0586 68	-0.0050 122	-0.0260 125	0.0025 139
O(3)	0.0760 92	0.1279 174	0.0573 74	-0.0059 177	-0.0011 127	0.0504 199
N(4)	0.0880 89	0.0032 85	0.0703 73	0.0048 123	0.0095 127	0.0172 137
C(5)	0.0543 90	0.1498 322	0.0755 113	-0.0260 351	0.0156 159	0.0153 298
C(6)	0.0814 102	0.0643 144	0.0541 75	0.0007 220	0.0235 140	0.0017 256
C(7)	0.0637 109	0.2045 368	0.0352 75	0.0213 259	0.0045 143	0.0269 335
C(8)	0.0465 69	0.0614 117	0.0449 67	0.0024 137	0.0077 108	0.0048 140
C(9)	0.0752 99	0.0534 132	0.0907 117	0.0609 274	0.0474 171	-0.0343 255
C(10)	0.0523 87	0.0696 169	0.0949 136	0.0458 223	0.0322 171	0.0196 169
C(11)	0.0477 76	0.0746 155	0.0725 101	0.0485 203	0.0098 136	0.0118 165
C(12)	0.0528 82	0.0515 143	0.0756 107	-0.0015 174	-0.0048 143	0.0043 153
C(13)	0.0356 69	0.0864 196	0.0641 95	0.0085 220	0.0306 127	0.0174 179

C(14)	0.0537 80	0.0537 135	0.0589 85	0.0012 153	0.0153 128	0.0321 150
C(15)	0.0806 121	0.0642 153	0.0645 103	0.0074 189	-0.0149 173	0.0183 215
C(16)	0.0884 109	0.0375 142	0.0663 92	0.0463 196	0.0379 158	0.0193 211
C(17)	0.1349 255	0.0811 233	0.1048 211	0.0409 375	0.0177 365	-0.0202 402
C(18)	0.0443 74	0.0780 147	0.0586 86	-0.0334 167	-0.0015 127	-0.0245 154

TABLE 4.4

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES

H	K	L	Fo	Fc
0	0	2	63.4	70.3
0	0	4	97.7	92.4
0	0	6	158.2	161.3
0	0	8	47.9	54.2
0	0	10	25.3	16.6
0	0	12	51.7	43.4
0	0	14	77.3	75.7
0	0	16	39.6	29.3
0	0	18	4.7	2.6
0	0	20	57.9	60.0
0	0	22	32.3	25.8
0	0	24	13.1	9.7
0	0	26	17.2	9.2
0	0	28	5.7	3.5
0	0	30	28.4	17.7
0	0	32	7.3	2.3
0	0	34	3.2	2.8
0	0	36	9.8	8.2
0	0	38	6.3	3.9
0	0-19		9.8	5.5
0	0-17		12.1	6.4
0	0-16		7.0	10.8
0	0-15		8.1	5.1
0	0-14		16.5	16.8
0	0-13		41.6	27.5
0	0-12		41.8	36.5
0	0-11		39.6	30.1
0	0-10		11.6	5.0
0	0-9		99.8	95.4
0	0-8		56.5	69.1
0	0-7		83.5	91.4
0	0-6		33.1	38.3
0	0-5		218.6	223.0
0	0-4		52.2	18.6
0	0-3		220.7	198.5
0	0-2		42.5	35.7
0	0-1		159.4	214.8
0	0	1	70.3	103.9
0	0	3	25.8	28.6
0	0	5	47.2	15.8
0	0	7	71.9	58.4
0	0	9	99.1	99.7
0	0	11	46.0	38.3
0	0	13	63.7	68.9
0	0	15	42.1	41.4
0	0	17	27.2	32.5
0	0	19	4.9	3.0
0	0	21	38.9	30.0
0	0	23	47.4	42.8
0	0	25	6.9	1.9
0	0	27	9.9	6.5
0	0	29	29.5	23.5
0	0	31	22.7	18.7
0	0	33	5.0	4.0
0	0	35	8.3	5.3
0	0	37	18.6	14.0
0	0-19		7.0	8.3
0	0-17		12.1	7.3
0	0-16		20.0	16.1
0	0-15		12.8	9.5
0	0-14		21.3	16.7
0	0-13		17.6	14.7
0	0-12		40.3	26.3
0	0-11		23.3	21.8
0	0-10		23.6	19.8
0	0-9		31.2	6.3
0	0-8		133.7	124.2
0	0-7		12.6	7.2
0	0-6		68.5	53.3
0	0-5		67.9	74.2
0	0-4		30.8	44.0
0	0-3		18.4	15.3
0	0-2		33.0	37.7
0	0-1		39.3	31.9
0	0	0	39.3	51.3
0	0	1	34.9	39.3
0	0	2	47.4	28.4
0	0	3	76.0	97.8
0	0	4	34.2	33.6
0	0	5	18.7	13.7
0	0	6	61.3	59.4
0	0	7	26.9	20.5
0	0	8	26.9	28.1
0	0	9	29.7	32.6
0	0	10	23.4	25.0
0	0	11	29.3	27.4
0	0	12	13.3	11.5
0	0	13	27.2	20.2
0	0	14	28.2	19.6
0	0	15	12.8	13.4
0	0	16	7.1	8.6
0	0	17	10.3	9.5
0	0	18	4.6	0.9
0	0-17		13.5	10.4
0	0-16		6.7	8.2
0	0-15		9.8	3.7
0	0-14		4.1	0.8
0	0-13		33.7	23.3
0	0-12		6.9	7.3
0	0-11		15.6	16.1
0	0-10		27.0	26.9
0	0-9		26.0	26.0
0	0-8		15.5	6.1
0	0-7		29.3	15.2
0	0-6		25.4	13.5
0	0-5		30.1	25.4
0	0-4		32.8	26.2
0	0-3		41.2	11.9
0	0-2		29.1	32.4
0	0-1		39.6	37.4
0	0	0	24.8	22.6
0	0	1	32.9	36.6
0	0	2	45.3	36.4
0	0	3	44.4	44.4
0	0	4	24.6	11.1
0	0	5	13.9	11.1
0	0	6	50.4	36.7
0	0	7	29.9	32.1
0	0	8	8.1	5.8
0	0	9	26.9	22.4
0	0	10	19.8	27.9
0	0	11	13.7	10.5
0	0	12	4.7	2.6
0	0	13	14.7	12.7
6	0	14	8.3	8.2
6	0	16	4.8	5.1
8	0	0	6.3	4.8
8	0-14		3.8	4.5
8	0-13		19.8	13.4
8	0-12		8.0	2.7
8	0-11		15.7	12.5
8	0-10		10.7	12.1
8	0-9		19.7	9.1
8	0-8		16.1	5.3
8	0-7		14.9	7.6
8	0-6		22.1	22.7
8	0-5		26.2	26.3
8	0-4		18.4	8.5
8	0-3		19.3	15.5
8	0-2		49.4	41.6
8	0-1		15.4	8.5
8	0	1	33.0	29.6
8	0	2	17.2	17.3
8	0	3	18.6	15.2
8	0	4	12.1	8.3
8	0	5	24.8	21.6
8	0	6	34.9	25.1
8	0	7	19.8	12.0
8	0	8	18.6	11.7
8	0	9	10.4	8.9
8	0	10	13.5	10.6
8	0-11		6.3	3.5
8	0-10		7.9	10.2
10	0-10		3.7	2.4
10	0-9		11.8	4.3
10	0-8		11.4	8.3
10	0-7		25.8	19.4
10	0-6		9.5	9.6
10	0-5		12.3	8.1
10	0-4		11.6	7.3
10	0-3		18.3	15.7
10	0-2		10.0	6.0
10	0-1		6.3	3.5
10	0	1	16.9	11.9
10	0	2	15.8	12.7
10	0	3	3.7	0.6
10	0	4	5.5	1.8
10	0	5	14.0	10.9
10	0	6	6.9	2.7
1	1-20		4.7	3.3
1	1-19		16.3	7.3
1	1-18		10.1	9.1
1	1-17		17.1	15.6
1	1-16		12.6	11.2
1	1-15		15.2	15.5
1	1-14		45.6	40.1
1	1-13		27.9	23.9
1	1-12		13.6	5.8
1	1-11		20.6	19.6
1	1-10		53.5	40.3
1	1-9		62.2	67.5
1	1-8		28.4	13.0
1	1-7		67.2	54.5
1	1-6		87.9	68.5
1	1-5		99.6	70.8
1	1-4		86.3	71.5
1	1-3		123.2	121.8
1	1-2		24.7	23.3
1	1-1		68.6	68.6
1	1	0	48.5	74.4
1	1	1	59.9	65.2
1	1	2	100.3	108.8
1	1	3	73.8	75.1
1	1	4	108.4	94.1
1	1	5	107.4	76.3
1	1	6	85.9	70.7
1	1	7	43.2	35.0
1	1	8	47.7	45.3
1	1	9	77.9	70.2
1	1	10	20.8	22.3
1	1	11	22.8	23.1
1	1	12	23.2	19.0
1	1	13	40.0	35.0
1	1	14	26.7	22.9
1	1	15	3.7	3.9
1	1	16	15.7	12.8
1	1	17	15.6	13.3
1	1	18	7.1	6.8
1	1	19	4.1	3.9
1	1-21		1.3	5.6
1	1-20		3.0	1.7
1	1-19		10.6	9.6
1	1-18		10.5	9.4
1	1-17		8.2	9.5
1	1-16		6.6	2.6
1	1-15		17.2	11.4
1	1-14		28.4	28.8
1	1-13		13.5	10.0
1	1-12		16.7	13.4
1	1-11		38.6	33.0
1	1-10		56.8	57.0
1	1-9		27.6	32.7
1	1-8		61.5	57.2
1	1-7		38.6	27.5
1	1-6		36.8	41.1
1	1-5		40.3	35.7
1	1-4		34.7	33.6
1	1-3		83.6	73.6
1	1-2		113.1	103.1
1	1-1		133.5	121.4
1	1	0	78.3	67.9
1	1	1	81.3	85.7
1	1	2	41.1	45.7
1	1	3	59.7	57.5
1	1	4	32.5	41.2
1	1	5	89.5	79.8
1	1	6	77.9	74.2
1	1	7	43.6	40.2
1	1	8	48.2	45.0
1	1	9	23.9	25.5
1	1	10	12.3	10.6
1	1	11	23.1	20.8
1	1	12	19.7	19.7
1	1	13	15.9	16.6
1	1	14	8.5	8.2
3	1	16	5.8	5.8
5	1	20	1.8	2.0
5	1-19		6.4	6.7
5	1-18		3.5	3.6
5	1-17		5.9	4.2
5	1-16		4.4	3.2
5	1-15		17.6	16.2
5	1-14		15.1	14.5
5	1-13		13.5	9.4
5	1-12		16.2	19.5
5	1-11		43.2	41.7
5	1-10		14.4	13.5
5	1-9		19.2	11.5
5	1-8		23.4	24.1
5	1-7		51.9	57.4
5	1-6		23.5	27.8
5	1-5		19.8	11.6
5	1-4		76.2	63.6
5	1-3		102.6	94.1
5	1-2		27.9	28.7
5	1-1		29.4	33.1
5	1	0	66.0	71.0
5	1	1	71.7	76.6
5	1	2	16.2	11.3
5	1	3	16.9	8.7
5	1	4	48.7	46.2
5	1	5	49.4	44.1
5	1	6	9.2	7.5
5	1	7	13.3	11.3
5	1	8	28.0	30.3
5	1	9	30.0	30.8
5	1	10	10.1	10.2
5	1	11	7.2	1.6
5	1	12	25.4	18.0
7	1	13	6.7	7.1
7	1	14	3.8	5.9
7	1	15	3.8	3.5
7	1	16	5.6	5.0
7	1	17	2.9	3.6
7	1	18	6.6	8.4
7	1-14		8.0	7.9
7	1-13		6.6	7.2
7	1-12		13.9	16.7
7	1-11		11.6	12.3
7	1-10		28.6	23.2
7	1-9		28.2	28.0
7	1-8		28.6	31.2
7	1-7		30.1	24.7
7	1-6		11.8	14.8
7	1-5		33.8	33.0
7	1-4		32.9	31.0
7	1-3		13.4	11.8
7	1-2		6.5	9.3
7	1-1		17.3	18.9
7	1	0	7.8	7.8
7	1	1	9.0	8.4
7	1	2	10.2	9.2
7	1	3	9.4	9.5
7	1	4	9.2	9.5
7	1	5	2.5	2.7
7	1	6	2.9	2.3
7	1	7	2.5	2.2
7	1	8	7.6	7.6
9	1-15		10.1	7.6
9	1-14		3.0	3.0
9	1-13		6.8	8.3
9	1-12		6.8	6.7
9	1-11		11.6	14.2
9	1-10		4.4	5.4
9	1-9		13.7	15.7
9	1-8		16.3	16.5
9	1-7		13.3	11.1
9	1-6		8.6	11.1
9	1-5		10.8	10.7
9	1-4		16.8	16.1
9	1-3		13.7	11.1
9	1-2		13.6	10.6
9	1-1		12.9	12.8
9	1	0	16.6	13.6
9	1	1	4.4	5.4
9	1	2	7.3	7.3
9	1	3	8.0	8.5
9	1	4	12.0	11.7
9	1	5	7.0	6.2
9	1	6	2.1	3.0
9	1	7	8.9	10.6
9	1	8	6.9	6.2
11	1-13		6.0	7.8
11	1-12		9.1	7.8
11	1-11		8.2	8.5
11	1-10		7.0	7.0
11	1-9		16.2	16.3
11	1-8		10.2	10.1
11	1-7		7.0	6.8
11	1-6		10.3	10.2
11	1-5		7.9	7.5
11	1-4		6.8	6.8
11	1-3		13.4	11.6
11	1-2		7.9	6.9
11	1-1		2.9	3.2
11	1	0	1.6	2.4
11	1	1	5.1	4.6
11	1	2	2.2	3.1
11	1	3	2.1	2.8
11	1	4	2.7	2.8
11	1	5	3.2	3.7
11	1	6	2.9	3.7
13	1-12		6.0	9.6
13	1-11		12.1	9.6
13	1-10		3.5	6.0
13	1-9		3.8	6.7
13	1-8		10.7	7.4
13	1-7		3.8	2.8
13	1-6		4.4	4.4
13	1-5		5.8	6.8
13	1-4		6.8	6.6
13	1-3		7.9	3.5
13	1-2		6.8	6.6
13	1-1		4.8	6.1
13	1	0	103.3	6.1
2	2	2	120.8	114.4
2	2	4	153.2	111.9
2	2	6	60.1	55.3
2	2	8	50.3	50.9
2	2	10	60.0	58.8
2	2	12	73.2	73.4

H	K	L	Fo	Fc
0	2	9	13.0	9.8
0	2	10	11.6	8.0
0	2	11	45.7	41.1
0	2	12	42.6	38.8
0	2	13	9.9	9.4
0	2	14	5.2	5.8
0	2	15	16.8	15.5
0	2	16	15.1	15.3
0	2	17	3.3	6.5
0	2	18	6.5	6.7
0	2	19	6.5	5.6
0	2-20		2.6	2.5
0	2-19		3.6	5.1
0	2-18		5.2	5.8
0	2-17		13.2	12.3
0	2-16		9.6	9.5
0	2-15		6.5	8.4
0	2-14		11.7	14.0
0	2-13		22.1	17.2
0	2-12		29.6	24.8
0	2-11		36.6	40.8
0	2-10		14.1	10.0
0	2-9		38.2	33.6
0	2-8		72.8	67.1
0	2-7		61.6	65.4
0	2-6		16.1	17.3
0	2-5		84.3	90.5
0	2-4		86.4	97.1
0	2-3		58.6	63.4
0	2-2		57.3	42.9
0	2-1		117.5	123.6
0	2	0	114.3	114.7
0	2	1	41.4	44.2
0	2	2	46.8	62.5
0	2	3	144.7	128.1
0	2	4	31.7	37.8
0	2	5	29.3	35.6
0	2	6	69.9	64.9
0	2	7	71.5	65.3
0	2	8	21.2	22.4
0	2	9	22.7	17.9
0	2	10	33.5	30.9
0	2	11	47.6	42.7
0	2	12	30.7	19.6
0	2	13	11.5	10.0
0	2	14	25.2	22.6
0	2	15	20.2	16.3
0	2	16	6.5	7.5
0	2	17	8.0	7.7
0	2	18	5.9	6.4
0	2-20		2.3	3.9
0	2-19		3.4	4.3
0	2-18		4.8	2.4
0	2-17		5.4	6.9
0	2-16		11.3	12.5
0	2-15		9.4	7.3
0	2-14		15.1	7.5
0	2-13		21.3	18.0
0	2-12		28.9	25.9
0	2-11		16.8	13.5
0	2-10		21.1	13.8
0	2-9		33.2	28.2
0	2-8		56.4	51.8
0	2-7		26.2	28.8
0	2-6		40.0	48.8
0	2-5		60.6	66.9
0	2-4		58.8	50.7
0	2-3		8.8	7.5
0	2-2		35.9	46.8
0	2-1		47.0	43.3
0	2	0	75.9	86.6
0	2	1	37.8	18.2
0	2	2	62.0	63.5
0	2	3	62.0	63.5
0	2	4	62.2	59.7
0	2	5	20.6	19.9
0	2	6	30.9	21.1
0	2	7	45.5	49.9
0	2	8	10.9	11.2
0	2	9	10.3	11.4
0	2	10	33.7	33.0
0	2	11	33.7	32.8
0	2	12	5.8	3.3
0	2	13	8.0	8.5
0	2	14	17.1	15.6
0	2	15	11.8	12.0
0	2	16	3.3	1.9
0	2	17	6.8	3.5
0	2-19		4.4	4.4
0	2-18		4.4	7.3
0	2-17		6.7	8.4
0	2-16		2.7	0.6
0	2-15		8.0	9.7
0	2-14		15.4	17.3
0	2-13		10.1	13.5
0	2-12		16.8	17.1
0	2-11		19.1	25.1
0	2-10		9.0	9.5
0	2-9		21.4	4.4
0	2-8		23.2	24.6
0	2-7		52.0	49.7
0	2-6		8.4	5.7
0	2-5		28.9	11.5
0	2-4		35.7	39.1
0	2-3		43.1	41.7
0	2-2		21.0	17.4
0	2-1		22.9	14.4
0	2	0	35.4	40.3
0	2	1	31.0	30.8
0	2	2	27.4	29.9
0	2	3	32.0	30.8
0	2	4	45.5	47.2
0	2	5	16.0	19.1
0	2	6	4.9	4.1
0	2	7	19.7	19.6
0	2	8	20.9	21.1
0	2	9	6.4	8.1
0	2	10	2.9	2.5
0	2	11	9.1	7.6
0	2	12	8.8	9.2
0	2	13	2.0	0.9
0	2	14	2.6	3.9
0	2	15	2.7	5.0

H	K	L	Fo	Fc
8	2-16		1.8	2.0
8	2-15		3.7	3.2
8	2-14		7.6	9.3
8	2-13		5.0	7.2
8	2-12		2.5	0.5
8	2-11		7.9	8.4
8	2-10		13.8	12.7
8	2-9		3.1	3.5
8	2-8		17.1	11.0
8	2-7		17.0	10.4
8	2-6		15.8	16.0
8	2-5		24.3	19.8
8	2-4		18.8	3.1
8	2-3		18.9	16.1
8	2-2		19.7	22.5
8	2-1		33.4	28.5
8	2	0	10.9	12.3
8	2	1	18.2	19.0
8	2	2	30.8	20.6
8	2	3	33.8	22.3
8	2	4	4.5	6.1
8	2	5	18.6	17.5
8	2	6	15.2	16.9
8	2	7	6.2	7.0
8	2	8	3.8	4.9
8	2	9	13.7	11.2
8	2	10	11.1	8.8
8	2	11	3.4	1.2
8	2	12	5.6	6.3
8	2	13	1.6	2.1
8	2	14	0.9	2.3
8	2	15	4.5	5.0
8	2	16	2.3	2.4
8	2	17	4.6	2.4
8	2-11		3.6	5.1
8	2-10		4.7	8.6
8	2-9		3.8	4.9
8	2-8		6.3	2.5
8	2-7		4.7	6.5
8	2-6		14.2	11.6
8	2-5		4.8	3.6
8	2-4		20.5	16.1
8	2-3		9.8	11.8
8	2-2		4.6	5.9
8	2-1		6.6	7.0
8	2	0	8.3	11.4
8	2	1	8.3	6.1
8	2	2	3.6	5.9
8	2	3	4.1	6.3
8	2	4	5.6	6.8
8	2	5	3.6	3.6
8	2	6	6.1	1.9
8	2	7	6.7	8.7
8	2	8	3.7	5.1
8	2	9	9.1	4.2
8	2	10	9.2	4.5
8	2	11	28.1	26.8
8	2	12	28.0	25.5
8	2	13	9.1	2.9
8	2	14	28.9	32.0
8	2	15	58.2	54.7
8	2	16	41.3	37.9
8	2	17	32.7	11.9
8	2	18	73.6	60.6
8	2	19	68.4	64.1
8	2-18		35.5	35.5
8	2-17		41.3	8.4
8	2-16		77.7	78.9
8	2-15		111.9	94.4
8	2-14		48.3	44.4
8	2-13		82.1	59.9
8	2-12		44.2	34.8
8	2-11		66.6	68.4
8	2-10		56.0	56.0
8	2-9		54.7	46.7
8	2-8		26.3	27.6
8	2-7		55.2	51.1
8	2-6		34.6	28.4
8	2-5		10.1	6.9
8	2-4		11.1	17.8
8	2-3		7.0	6.2
8	2-2		21.1	9.3
8	2-1		17.0	10.4
8	2	0	8.6	6.2
8	2	1	10.4	11.7
8	2	2	12.0	10.8
8	2	3	7.0	6.8
8	2	4	9.1	7.8
8	2	5	8.2	8.5
8	2	6	10.2	10.3
8	2	7	6.9	6.2
8	2	8	6.8	7.0
8	2	9	2.9	4.1
8	2	10	5.0	5.2
8	2	11	9.7	9.7
8	2	12	8.8	11.1
8	2	13	10.7	10.7
8	2	14	13.8	11.7
8	2	15	19.3	16.9
8	2	16	9.5	9.5

H	K	L	Fo	Fc
3	3	16	13.6	12.6
3	3	17	2.9	4.7
3	3	18	4.8	6.9
3	3	19	6.9	7.2
3	3	20	1.2	1.8
3	3-17		4.3	3.3
3	3-16		15.4	15.4
3	3-15		12.9	13.3
3	3-14		6.4	3.1
3	3-13		12.0	7.5
3	3-12		19.9	21.0
3	3-11		36.8	35.1
3	3-10		7.7	7.8
3	3-9		38.7	39.0
3	3-8		44.3	42.9
3	3-7		16.0	17.1
3	3-6		5.5	6.9
3	3-5		11.1	6.9
3	3-4		42.6	28.7
3	3-3		65.0	64.4
3	3-2		11.7	14.7
3	3-1		24.2	23.5
3	3	0	40.8	39.8
3	3	1	71.7	59.8
3	3	2	13.0	14.7
3	3	3	39.1	44.9
3	3	4	36.0	36.1
3	3	5	11.2	12.7
3	3	6	9.0

H	K	L	Fo	Fc
0	0	2	10.8	10.8
0	0	4	11.0	11.8
0	0	6	18.6	18.4
0	0	8	11.2	11.2
0	0	10	10.2	9.7
0	0	12	16.4	16.2
0	0	14	4.5	4.5
0	0	16	11.4	11.6
0	0	18	36.5	34.1
0	0	20	26.3	25.1
0	0	22	36.5	34.6
0	0	24	44.2	40.2
0	0	26	22.9	22.9
0	0	28	5.9	5.6
0	0	30	26.5	26.5
0	0	32	13.9	13.9
0	0	34	3.3	3.3
0	0	36	39.7	39.7
0	0	38	52.7	52.7
0	0	40	33.3	33.3
0	0	42	20.9	20.9
0	0	44	36.2	36.2
0	0	46	12.8	12.8
0	0	48	12.1	12.1
0	0	50	4.1	4.1
1	0	1	7.8	7.8
1	0	3	29.3	29.3
1	0	5	33.6	33.7
1	0	7	19.1	19.1
1	0	9	30.5	30.5
1	0	11	17.0	17.0
1	0	13	30.6	30.6
1	0	15	21.8	21.8
1	0	17	41.2	41.2
1	0	19	46.6	46.8
1	0	21	19.2	19.2
1	0	23	17.7	17.7
1	0	25	10.1	10.1
1	0	27	29.6	29.6
1	0	29	16.2	16.2
1	0	31	10.9	10.8
1	0	33	15.1	15.1
1	0	35	5.3	5.3
1	0	37	9.6	9.6
1	0	39	16.2	16.2
1	0	41	10.2	10.2
1	0	43	14.0	14.0
1	0	45	6.2	6.2
1	0	47	6.2	6.2
1	0	49	5.6	5.6
2	0	0	42.1	42.4
2	0	2	40.2	38.6
2	0	4	16.4	11.5
2	0	6	16.4	12.0
2	0	8	41.5	44.0
2	0	10	22.8	15.7
2	0	12	10.9	8.7
2	0	14	8.1	9.4
2	0	16	31.3	29.0
2	0	18	11.3	7.7
2	0	20	4.1	4.1
2	0	22	8.0	4.4
2	0	24	10.8	10.2
2	0	26	9.5	9.1
2	0	28	3.5	4.6
2	0	30	4.0	3.2
2	0	32	7.8	6.4
2	0	34	14.4	13.9
2	0	36	6.5	8.6
2	0	38	14.8	12.1
2	0	40	12.6	10.4
2	0	42	15.0	12.4
2	0	44	15.5	14.3
2	0	46	26.5	24.3
2	0	48	17.6	15.9
2	0	50	34.8	30.0
3	0	1	26.7	29.7
3	0	3	18.0	19.1
3	0	5	12.5	11.2
3	0	7	6.9	4.7
3	0	9	2.2	3.9
3	0	11	10.4	10.3
3	0	13	12.5	12.5
3	0	15	6.8	6.8
3	0	17	5.7	5.7
3	0	19	10.7	10.7
3	0	21	16.7	16.7
3	0	23	13.5	13.5
3	0	25	15.5	15.5
3	0	27	10.0	10.0
3	0	29	11.8	11.8
3	0	31	9.6	9.6
3	0	33	15.2	15.2
3	0	35	10.0	10.0
3	0	37	11.6	11.6
3	0	39	4.7	4.7
3	0	41	9.1	9.1
3	0	43	6.8	6.8
3	0	45	5.6	5.6
3	0	47	5.6	5.6
4	0	0	117.8	113.5
4	0	2	16.9	16.1
4	0	4	21.9	19.6
4	0	6	21.9	19.6
4	0	8	17.4	15.9
4	0	10	24.4	20.1
4	0	12	22.6	22.6
4	0	14	16.4	16.2
4	0	16	14.9	15.2
4	0	18	18.3	18.3
4	0	20	16.7	15.7
4	0	22	13.5	10.4
4	0	24	3.9	4.8
4	0	26	30.5	30.7
4	0	28	4.2	4.2
4	0	30	4.8	1.9
4	0	32	6.8	3.6
4	0	34	5.9	5.9
4	0	36	5.1	3.4
4	0	38	4.8	2.9
4	0	40	4.2	4.9
4	0	42	8.5	9.3
4	0	44	8.5	9.3
4	0	46	11.3	11.3
4	0	48	8.9	10.1
4	0	50	4.4	6.4
5	0	1	17.0	16.0
5	0	3	22.7	20.5
5	0	5	9.1	7.7
5	0	7	34.1	26.0
5	0	9	38.3	30.5
5	0	11	22.4	17.9
5	0	13	11.4	9.3
5	0	15	36.4	35.1
5	0	17	28.8	30.9
5	0	19	8.9	10.1
5	0	21	26.5	28.6
5	0	23	8.8	9.9
5	0	25	12.2	9.4
5	0	27	10.5	14.7
5	0	29	7.4	7.8
5	0	31	5.6	6.8
5	0	33	6.2	6.2
5	0	35	6.2	9.5
5	0	37	3.8	5.6
5	0	39	2.7	5.4
5	0	41	5.7	4.0
5	0	43	5.6	6.8
5	0	45	8.6	7.0
5	0	47	3.9	3.9
6	0	2	8.8	8.8
6	0	4	15.9	15.9
6	0	6	13.0	13.0
6	0	8	17.9	17.9
6	0	10	15.6	15.6
6	0	12	11.9	11.9
6	0	14	14.0	14.0
6	0	16	12.3	12.3
6	0	18	12.9	12.9
6	0	20	10.8	10.8
6	0	22	11.8	11.8
6	0	24	18.4	18.4
6	0	26	20.6	20.6
6	0	28	11.5	7.0
6	0	30	6.7	5.6
6	0	32	11.1	14.1
6	0	34	9.0	10.3
6	0	36	6.1	4.2
6	0	38	9.1	5.0
6	0	40	4.1	4.0
6	0	42	9.5	11.8
6	0	44	2.8	2.8
6	0	46	2.8	2.8
6	0	48	10.6	10.8
7	0	1	22.7	26.2
7	0	3	20.0	19.1
7	0	5	6.2	6.8
7	0	7	27.2	21.9
7	0	9	59.4	43.2
7	0	11	20.9	16.5
7	0	13	17.6	12.7
7	0	15	32.8	30.5
7	0	17	39.0	39.2
7	0	19	34.5	27.8
7	0	21	39.5	38.8
7	0	23	20.0	20.9
7	0	25	15.2	14.2
7	0	27	4.7	5.0
7	0	29	7.7	8.3
7	0	31	2.9	5.7
7	0	33	10.9	7.8
7	0	35	12.1	10.6
7	0	37	7.0	9.7
7	0	39	2.5	1.7
7	0	41	21.5	20.6
7	0	43	13.2	19.8
7	0	45	10.4	12.2
7	0	47	22.3	19.8
7	0	49	13.3	13.0
8	0	0	24.6	17.7
8	0	2	30.9	28.5
8	0	4	8.7	8.9
8	0	6	8.4	7.5
8	0	8	2.1	1.8
8	0	10	12.5	12.1
8	0	12	10.8	11.9
8	0	14	5.5	5.6
8	0	16	13.7	14.9
8	0	18	2.9	2.2
8	0	20	3.6	3.2
8	0	22	8.0	7.8
8	0	24	6.3	4.1
8	0	26	3.5	3.3
8	0	28	2.9	3.1
8	0	30	3.4	3.4
8	0	32	6.9	5.8
8	0	34	3.3	3.3
8	0	36	3.6	4.6
8	0	38	3.0	3.0
8	0	40	3.0	3.7
8	0	42	3.5	3.5
8	0	44	2.6	2.6
8	0	46	1.6	2.5
8	0	48	5.5	5.4
9	0	1	4.5	5.1
9	0	3	6.5	5.5
9	0	5	2.1	1.8
9	0	7	13.8	15.7
9	0	9	17.5	22.6
9	0	11	23.1	22.7
9	0	13	22.6	22.3
9	0	15	14.9	15.2
9	0	17	18.3	18.3
9	0	19	16.7	15.7
9	0	21	13.5	10.4
9	0	23	3.9	4.8
9	0	25	30.5	30.7
9	0	27	4.2	4.2
9	0	29	4.8	1.9
9	0	31	6.8	3.6
9	0	33	5.9	5.9
9	0	35	5.1	3.4
9	0	37	4.8	2.9
9	0	39	4.2	4.9
9	0	41	8.5	9.3
9	0	43	8.5	9.3
9	0	45	11.3	11.3
9	0	47	8.9	10.1
10	0	0	9.9	11.7
10	0	2	9.7	9.7
10	0	4	9.2	9.2
10	0	6	6.0	6.0
10	0	8	17.4	17.4
10	0	10	19.1	19.7
10	0	12	2.0	2.0
10	0	14	3.9	4.4
10	0	16	9.6	9.6
10	0	18	10.4	10.4
10	0	20	9.9	9.4
10	0	22	10.2	9.9
10	0	24	8.0	8.0
10	0	26	4.5	4.5
10	0	28	5.7	5.7
10	0	30	8.0	8.0
10	0	32	23.6	23.6
10	0	34	5.9	5.9
10	0	36	10.6	10.6
10	0	38	2.2	2.2
10	0	40	5.5	5.7
10	0	42	4.9	4.9
10	0	44	7.6	7.8
10	0	46	6.9	6.9
10	0	48	10.4	10.4
11	0	1	10.5	9.7
11	0	3	16.9	15.0
11	0	5	7.7	7.3
11	0	7	8.0	8.0
11	0	9	10.3	11.7
11	0	11	18.0	11.9
11	0	13	8.2	6.8
11	0	15	9.4	9.4
11	0	17	11.3	10.3
11	0	19	10.7	10.9
11	0	21	9.8	10.0
11	0	23	2.6	1.2
11	0	25	1.8	2.4
11	0	27	2.6	4.2
11	0	29	1.6	0.7
11	0	31	1.5	5.2
11	0	33	4.7	4.4
11	0	35	13.2	9.0
11	0	37	2.2	4.7
11	0	39	5.1	5.3
11	0	41	3.7	4.7
11	0	43	1.0	0.4
11	0	45	4.2	5.3
12	0	0	12.4	12.9
12	0	2	11.4	10.6
12	0	4	10.6	10.6
12	0	6	16.1	16.0
12	0	8	15.1	15.2
12	0	10	8.8	8.8
12	0	12	19.5	19.5
12	0	14	3.9	3.9
12	0	16	7.7	7.7
12	0	18	22.0	22.0
12	0	20	4.6	4.6
12	0	22	2.6	2.6
12	0	24	2.6	2.6
12	0	26	2.6	2.6
12	0	28	2.6	2.6
12	0	30	2.6	2.6
12	0	32	2.6	2.6
12	0	34	2.6	2.6
12	0	36	2.6	2.6
12	0	38	2.6	2.6
12	0	40	2.6	2.6
12	0	42	2.6	2.6
12	0	44	2.6	2.6
12	0	46	2.6	2.6
12	0	48	2.6	2.6
13	0	1	2.6	2.6
13	0	3	2.6	2.6
13	0	5	2.6	2.6
13	0	7	2.6	2.6
13	0	9	2.6	2.6
13	0	11	2.6	2.6
13	0	13	2.6	2.6
13	0	15	2.6	2.6
13	0	17	2.6	2.6
13	0	19	2.6	2.6
13	0	21	2.6	2.6
13	0	23	2.6	2.6
13	0	25	2.6	2.6
13	0	27	2.6	2.6
13	0	29	2.6	2.6
13	0	31	2.6	2.6
13	0	33	2.6	2.6
13	0	35	2.6	2.6
13	0	37	2.6	2.6
13	0	39	2.6	2.6
13	0	41	2.6	2.6
13	0	43	2.6	2.6
13	0	45	2.6	2.6
13	0	47	2.6	2.6
14	0	0	2.6	2.6
14	0	2	2.6	2.6
14	0	4	2.6	2.6
14	0	6	2.6	2.6
14	0	8	2.6	2.6
14	0	10	2.6	2.6
14	0	12	2.6	2.6
14	0	14	2.6	2.6
14	0	16	2.6	2.6
14	0	18	2.6	2.6
14	0	20	2.6	2.6
14	0	22	2.6	2.6
14	0	24	2.6	2.6
14	0	26	2.6	2.6
14	0	28	2.6	2.6
14	0	30	2.6	2.6
14	0	32	2.6	2.6
14	0	34	2.6	2.6
14	0	36	2.6	2.6
14	0	38	2.6	2.6
14	0	40	2.6	2.6
14	0	42	2.6	2.6
14	0	44	2.6	2.6
14	0	46	2.6	2.6
14	0	48	2.6	2.6
15	0	1	2.6	2.6
15	0	3	2.6	2.6
15	0	5	2.6	2.6
15	0	7	2.6	2.6
15	0	9	2.6	2.6
15	0	11	2.6	2.6
15	0	13	2.6	2.6
15	0	15	2.6	2.6
15	0	17	2.6	2.6
15	0	19	2.6	2.6
15	0	21	2.6	2.6
15	0	23	2.6	2.6
15	0	25	2.6	2.6
15	0	27	2.6	2.6
15	0	29	2.6	2.6
15	0	31	2.6	2.6
15	0	33	2.6	2.6
15	0	35	2.6	2.6
15	0	37	2.6	2.6
15	0	39	2.6	2.6
15	0	41	2.6	2.6
15	0	43	2.6	2.6
15	0	45	2.6	2.6
15	0	47	2.6	2.6
16	0	0	2.6	2.6
16	0	2	2.6	2.6
16	0	4	2.6	2.6
16	0	6	2.6	2.6
16	0	8	2.6	2.6
16	0	10	2.6	2.6
16	0	12	2.6	2.6
16	0	14	2.6	2.6
16	0	16	2.6	2.6
16	0	18	2.6	2.6
16	0	20	2.6	2.6
16	0	22	2.6	2.6
16	0	24	2.6	2.6
16	0	26	2.6	2.6
16	0	28	2.6	2.6
16	0	30	2.6	2.6
16	0	32	2.6	2.6
16	0	34	2.6	2.6
16	0	36	2.6	2.6
16	0	38	2.6	2.6
16	0	40	2.6	2.6
16	0	42	2.6	2.6
16	0	44	2.6	2.6
16	0	46	2.6	2.6
16	0	48	2.6	2.6
17	0	1	2.6	2.6
17	0	3	2.6	2.6
17	0	5	2.6	2.6
17	0	7	2.6	2.6
17	0	9	2.6	2.6
17	0	11	2.6	2.6
17	0	13	2.6	2.6
17	0	15	2.6	2.6
17	0	17	2.6	2.6
17	0	19	2.6	2.6
17	0	21	2.6	2.6
17	0	23	2.6	2.6
17	0	25	2.6	2.6
17	0	27	2.6	2.6
17	0	29	2.6	2.6
17	0	31	2.6	2.6
17	0	33	2.6	2.6
17	0	35	2.6	2.6
17	0	37	2.6	2.6
17	0	39	2.6	2.6
17	0	41	2.6	2.6
17	0	43	2.6	2.6
17	0	45	2.6	2.6
17	0	47	2.6	2.6
18	0	0	2.6	2.6
18	0	2	2.6	2.6
18	0	4	2.6	2.6
18	0	6	2.6	2.6
18	0	8	2.6	2.6
18	0	10	2.6	2.6
18	0	12	2.6	2.6
18	0	14	2.6	2.6
18	0	16	2.6	2.6
18	0	18	2.6	2.6
18	0	20	2.6	2.6
18	0	22	2.6	2.6
18	0	24	2.6	2.6
18	0	26	2.6	2.6
18	0	28	2.6	2.6
18	0	30	2.6	2.6
18	0	32	2.6	2.6
18	0	34	2.6	2.6
18	0	36	2.6	2.6
18	0	38	2.6	2.6
18	0	40	2.6	2.6
18	0	42	2.6	2.6
18	0	44	2.6	2.6
18	0	46	2.6	2.6
18	0	48	2.6	2.6
19	0	1	2.6	2.6
19	0	3	2.6	2.6
19	0	5	2.6	2.6
19	0	7	2.6	2.6
19	0	9	2.6	2.6
19	0	11	2.6	2.6
19	0	13	2.6	2.6
19	0	15	2.6	2.6
19	0	17	2.6	2.6
19	0	19	2.6	2.6
19	0	21	2.6	2.6
19	0	23	2.6	2.6
19	0	25	2.6	2.6
19	0	27	2.6	2.6
19	0	29	2.6	2.6
19	0	31	2.6	2.6
19	0	33	2.6	2.6
19	0	35	2.6	2.6
19	0	37	2.6	2.6
19	0	39	2.6	2.6
19	0	41	2.6	2.6
19	0	43	2.6	2.6
19	0	45	2.6	2.6
19	0	47	2.6	2.6
20	0	0	2.6	2.6
20	0	2	2.6	2.6
20	0	4	2.6	2.6
20	0	6	2.6	2.6
20	0	8	2.6	2.6
20	0	10	2.6	2.6
20	0	12	2.6	2.6
20	0	14	2.6	2.6
20	0	16	2.6	2.6
20	0	18	2.6	2.6
20	0	20	2.6	2.6
20	0	22	2.6	2.6
20	0	24	2.6	2.6
20	0	26	2.6	2.6
20	0	28	2.6	2.6
20	0	30	2.6	2.6
20	0	32	2.6	2.6
20	0	34	2.6	2.6
20	0	36	2.6	2.6
20	0	38	2.6	2.6
20	0	40	2.6	2.6
20	0	42	2.6	2.6
20	0	44	2.6	2.6
20	0	46	2.6	2.6
20	0	48	2.6	2.6

TABLE 4.5

ORTHOGONAL COORDINATES AND E.S.D.S.

ATOM	X'	Y	Z'
Br(1)	2.663 ± 2	4.973 ± 0	1.359 ± 2
O(2)	4.992 ± 16	0.732 ± 17	4.902 ± 16
O(3)	6.825 ± 18	1.176 ± 26	6.025 ± 17
N(4)	2.271 ± 17	0.299 ± 18	1.819 ± 17
C(5)	1.769 ± 21	0.335 ± 48	3.160 ± 24
C(6)	2.842 ± 21	0.007 ± 34	4.229 ± 18
C(7)	3.605 ± 23	-1.166 ± 47	3.903 ± 20
C(8)	4.144 ± 15	-1.253 ± 22	2.536 ± 16
C(9)	3.737 ± 20	0.154 ± 32	1.854 ± 22
C(10)	4.365 ± 20	1.186 ± 26	2.639 ± 26
C(11)	3.892 ± 17	1.323 ± 27	4.188 ± 22
C(12)	5.893 ± 18	1.695 ± 23	5.434 ± 23
C(13)	5.690 ± 16	3.033 ± 31	5.273 ± 20
C(14)	4.397 ± 17	3.503 ± 22	4.991 ± 19
C(15)	3.383 ± 24	2.596 ± 27	4.579 ± 25
C(16)	4.177 ± 21	5.148 ± 27	4.926 ± 20
C(17)	1.810 ± 43	1.411 ± 45	0.916 ± 42
C(18)	1.566 ± 17	-1.026 ± 24	1.180 ± 19

TABLE 4.6

BOND LENGTHS AND E.S.D.S.

O(2) - C(11)	1.438 ± 26 Å	C(7) - C(8)	1.472 ± 26 Å
O(2) - C(12)	1.422 ± 27	C(8) - C(9)	1.615 ± 36
O(3) - C(12)	1.219 ± 28	C(9) - C(10)	1.441 ± 37
N(4) - C(5)	1.432 ± 29	C(10)- C(11)	1.625 ± 33
N(4) - C(9)	1.473 ± 26	C(11)- C(15)	1.425 ± 37
N(4) - C(17)	1.505 ± 47	C(12)- C(13)	1.363 ± 39
N(4) - C(18)	1.631 ± 29	C(13)- C(14)	1.405 ± 26
C(5) - C(6)	1.551 ± 32	C(14)- C(15)	1.422 ± 32
C(6) - C(7)	1.436 ± 51	C(14)- C(16)	1.661 ± 35
C(6) - C(11)	1.684 ± 38		

TABLE 4.7

INTERBOND ANGLES AND E.S.D.S.

C(11)- O(2) - C(12)	113.1 ± 18°	C(9) - C(10)- C(11)	116.9 ± 19°
C(5) - N(4) - C(9)	109.2 ± 16	O(2) - C(11)- C(6)	98.2 ± 18
C(5) - N(4) - C(17)	115.8 ± 26	O(2) - C(11)- C(10)	102.5 ± 15
C(5) - N(4) - C(18)	103.7 ± 21	O(2) - C(11)- C(15)	120.3 ± 20
C(9) - N(4) - C(17)	113.1 ± 23	C(6) - C(11)- C(10)	98.0 ± 16
C(9) - N(4) - C(18)	111.1 ± 17	C(6) - C(11)- C(15)	118.0 ± 17
C(17)- N(4) - C(18)	103.4 ± 21	C(10)- C(11)- C(15)	116.1 ± 21
N(4) - C(5) - C(6)	113.4 ± 18	O(2) - C(12)- O(3)	112.2 ± 21
C(5) - C(6) - C(7)	112.6 ± 23	O(2) - C(12)- C(13)	121.8 ± 18
C(5) - C(6) - C(11)	104.4 ± 24	O(3) - C(12)- C(13)	126.0 ± 22
C(7) - C(6) - C(11)	107.5 ± 19	C(12)- C(13)- C(14)	119.3 ± 20
C(6) - C(7) - C(8)	117.0 ± 27	C(13)- C(14)- C(15)	120.1 ± 22
C(7) - C(8) - C(9)	104.4 ± 22	C(13)- C(14)- C(16)	117.5 ± 19
N(4) - C(9) - C(8)	110.3 ± 19	C(15)- C(14)- C(16)	121.8 ± 18
N(4) - C(9) - C(10)	112.1 ± 21	C(11)- C(15)- C(14)	113.3 ± 20
C(8) - C(9) - C(10)	106.5 ± 18		

TABLE 4.8

INTERMOLECULAR CONTACTS BELOW 4 Å

O(3).....C(16)	v	3.34 Å	C(12)....C(14)	iii	3.81 Å
C(16)....O(3)	vii	3.42	Br(1)....C(5)	iv	3.82
O(3).....C(15)	iii	3.46	C(13)....C(15)	iii	3.83
C(13)....C(14)	iii	3.49	C(13)....C(7)	iv	3.85
C(13)....O(3)	vii	3.50	C(18)....Br(1)	i	3.87
C(13)....C(6)	iv	3.56	O(2).....O(2)	iii	3.89
C(7).....C(16)	i	3.59	C(16)....C(5)	iv	3.89
O(3).....C(6)	iii	3.60	Br(1)....C(17)	vi	3.90
C(12)....C(12)	iii	3.69	C(12)....C(13)	iii	3.92
O(2).....O(3)	iii	3.69	C(18)....C(18)	ii	3.92
O(3).....C(11)	iii	3.69	C(16)....C(16)	iii	3.93
C(13)....C(13)	iii	3.70	C(16)....C(6)	iv	3.96
C(14)....C(14)	iii	3.71	C(8).....Br(1)	i	3.97
C(12)....C(15)	iii	3.75	O(3).....C(14)	iii	3.97
O(2).....C(12)	iii	3.77	C(14)....O(3)	vii	3.99
C(12)....C(16)	v	3.79			

Roman numerals refer to the transformations of the fractional coordinates given in Table 4.2.

i	$x, -1 + y, z;$		v	$\frac{1}{2} + x, -\frac{1}{2} + y, z;$	
ii	$-x, y, -z;$		vi	$\frac{1}{2} - x, \frac{1}{2} + y, -z;$	
iii	$1 - x, y, 1 - z;$		vii	$1\frac{1}{2} - x, \frac{1}{2} + y, 1 - z;$	
iv	$\frac{1}{2} + x, \frac{1}{2} + y, z;$				

The transformations are applied to the coordinates of the second atom in each case.

TABLE 4.9

MEAN MOLECULAR PLANES

(A) ATOMS DEFINING PLANES

PLANE NO.	ATOMS DEFINING PLANE
1	N(4), C(5), C(6) and C(9)
2	C(6), C(7), C(8) and C(9)
3	C(6), C(9), C(10) and C(11)
4	O(2), O(3), C(11), C(12) and C(13)
5	C(12), C(13), C(14), C(15) and C(16)

(B) PLANE EQUATIONS

PLANE NO.	P	Q	R	S	RMS D
1	-0.1432	-0.9852	-0.0938	-0.8352	0.037
2	-0.8411	-0.4258	-0.3335	-3.8168	0.016
3	-0.7482	0.6125	-0.2551	-3.1897	0.018
4	0.5296	-0.0220	-0.8479	-1.5231	0.004
5	0.3032	0.0195	-0.9527	-3.3126	0.044

P, Q and R are the direction cosines of the plane normal, S is the plane to origin distance and RMS D is the root mean square deviation of the atoms defining the plane, from the plane, in Angstroms. The plane equation is then

$$PX + QY + RZ = S$$

where X, Y and Z are coordinates in Angstroms referred to standard orthogonal axes.

(C) DEVIATIONS FROM PLANES (Å)

PLANE NO. ATOM	1	2	3	4	5
Br(1)	-	-	-	-	-
O(2)	-	-	-	-0.005	0.170
O(3)	-	-	-	0.003	-0.335
N(4)	0.045	1.173	1.209	-	-
C(5)	-0.045	1.133	1.266	-	-
C(6)	0.025	0.013	-0.012	-0.558	0.145
C(7)	1.101	-0.021	-1.217	-	-
C(8)	1.238	0.019	-1.325	-	-
C(9)	-0.026	-0.010	0.015	-	-
C(10)	-1.206	-1.240	-0.023	1.571	2.145
C(11)	-1.418	-1.417	0.020	0.004	0.528
C(12)	-	-	-	-0.001	-0.045
C(13)	-	-	-	-0.001	0.073
C(14)	-	-	-	-0.457	-0.041
C(15)	-	-	-	-0.625	0.027
C(16)	-	-	-	-0.555	-0.014
C(17)	-	-	-	-	-
C(18)	-	-	-	-	-

(D) DIHEDRAL ANGLES

PLANE A	PLANE B	∠ AB
1	2	55.2°
1	3	61.8
1	4	88.6
1	5	88.5
2	3	63.0
2	4	81.2
2	5	86.9
3	4	78.9
3	5	88.4
4	5	14.5

4.4 Discussion

Although the main structural features of the alkaloid have been determined, the stereochemistry of the attachment of the lactone group was not unambiguously established (Page and Pinder, 1964). The X-ray analysis of the methobromide derivative of dioscorine was undertaken to confirm the structure assigned and to establish clearly the relative configuration of the lactone ring linkage.

The limited accuracy achieved in this analysis precludes discussion of the individual bond lengths, valence angles and the effects that small changes in these features would have on the molecular geometry. The agreement between the observed and final calculated structure amplitudes (Table 4.4), however, indicates that the gross molecular structure is correct and that limited information concerning the conformation of the lactone ring may be derived.

Dioscorine consists of an iso-quinuclidine residue to which an unsaturated δ - lactone is spiro linked. The individual values of the bond lengths and valence angles obtained for the molecule do not differ significantly from accepted values apart from the angles at C(11), where it would be expected that bond deformation would occur to reduce the strain in this region of the molecule due to the spiro linkage. The angles at C(11) fall into two categories; those less than the tetrahedral angle, O(2)-C(11)-C(6) (98°), O(2)-C(11)-C(10) (103°) and C(6)-C(11)-C(10) (98°) and those greater than the

tetrahedral angle, O(2)-C(11)-C(15) (120°), C(6)-C(11)-C(15) (118°) and C(10)-C(11)-C(15) (116°).

The lactone ring adopts a flattened half-boat conformation in which carbon atoms C(14) and C(15) of the lactone ring are displaced to the same side of the plane containing the lactone group. Atoms O(2), O(3), C(11), C(12) and C(13) are strictly planar. The deviations of the atoms from the best plane through these atoms are all less than 0.005 Å and the average estimated standard deviations of the positional parameters of these atoms is 0.02 Å. Atoms C(14), C(15) and C(16) are out of the best plane through these atoms by 0.46, 0.63 and 0.56 Å respectively, on the same side of C(11) as C(6).

Mathieson, (1963) has shown that a planar constraint on four atoms of a six-membered ring can lead to either a half-boat or a half-chair conformation and in the case of a lactone group, it has been inferred that this constraint imposes a half-boat conformation on the six-membered ring. However Cheung et al., (1965) have suggested that δ - lactones adopt the half-chair conformation if free to do so and that the half-boat conformation only arises in response to special circumstances. In the present case, the inclusion of a second planar group within the six-membered ring precludes the half-chair conformation from consideration on steric grounds.

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